A GENERAL RELATION OF ELECTRO-MOTIVE FORCE TO EQUIVALENT VOLUME AND MOLECULAR VELOCITY OF SUBSTANCES.

By Dr. G. GORE, F.R.S.

3 9 7 1 1

IV.—*A General Relation of Electromotive Force to Equivalent
Volume and Molecular Velocity of Substances.*

By Dr. G. Gore, F.R.S.

[Read before the Society, February 17th, 1892.]

3 9 7 1 1

In a research on " The Relations of Volta-Electromotive Force
to Latent Heat, &c., of Electrolytes " (Phil. Mag., August,
1891, p. 165), I have shown that in 18 out of 19 cases of
dilution of electrolytes with water, on measuring the electro-
motive force excited by immersing a simple voltaic couple
separately in the water, and in the undiluted and diluted
electrolytes, an excess or *gain* of that force was produced by
the diluted liquid above that of the *mean* amount as calculated
from the separate amounts excited by the water and the
undiluted liquid, and that the gain was usually greatest with
acids, less with neutral salts, and least with alkalies ; and in a
subsequent research on " A Method of Measuring Loss of
Energy Due to Chemical Union, &c." (Phil. Mag., January,
1892, p. 28), I have further shown by a similar method that
when the ingredients of two electrolytes mix together with
strong chemical union, a *loss* of *mean* amount of electromotive
force occurs, and that when they mix without any degree of
such union, as in cases of pure dilution by means of water, a

gain of such force nearly always takes place.   The same kind of general effect was obtained if the kind of positive metal of the voltaic couple was varied.

In the present research I have specially investigated the influence of *dilution*, and have ascertained the effects upon the *mean* amount of electromotive force of the voltaic couple : first, of simple dilution of the electrolyte with water ; second, of liquefaction of the positive metal by mercury to form an amalgam ; third, of dilution of the amalgam by additional mercury ; and from the results obtained I have been led to infer an explanation of the origin of the current.   As the two most important substances in producing the current are the positive metal and the negative constituent of the electrolyte, the investigation was chiefly confined to them ; additional experiments were, however, made to ascertain the influence of liquefaction and dilution of the negative metal, of dilution of one solid metal by means of another, and of other circumstances, upon the *mean* amount of electromotive force of the couple.

The method of examination and measurement employed in the case of electrolytes has already been fully described (*ibid.*), and is briefly as follows :—Measure the electromotive force of a simple zinc platinum voltaic couple, first in water alone ;   second, in a suitably dilute solution of the electrolytic substance ;   and third, in the mixture of the two. Multiply the electromotive force of the couple in water by the weight of the water, and that of the undiluted aqueous solution by the weight of the solution ; add the two products together and divide the sum by the total weights of the two liquids, in order to obtain the calculated *mean* amount of electromotive force of the couple in the mixture.   Subtract this amount from that obtained by experiment with the mixture (or the reverse, as the case may be), and the difference is the amount of gain (or loss) of *mean* amount of electromotive force of the two mixed substances attending the dilution.   The method adopted of measuring the electromotive force was that of opposition and balance of the current from the voltaic couple by one from a

thermoelectric pile of about 800 pairs of iron and German silver wires (see Proc. Birm. Phil. Soc., vol. iv., p. 130; Electrician, vol. xii., p. 414), with a suitable galvanometer in the circuit. A similar method was employed to ascertain the change of *mean* amount of electromotive force caused by *liquefaction* of the positive metal in mercury, *i.e.* : first, the electromotive force of the solid metal with platinum in the given electrolyte was measured ; second, that of mercury with platinum was then found, and the mean amount of the two quantities calculated ; and third, that of the amalgam with platinum was also measured. The method of ascertaining the effect of *dilution* of the positive metal amalgam was similar. In determining the effects of liquefaction and dilution of the negative metal by means of mercury the same method was used, a constant positive plate of zinc being employed. The same method which enables us to measure the changes of mean amount of electromotive force, necessarily also enables us to examine, and in some degree to measure, the accompanying losses and gains of chemical energy ; of freedom of molecular motion, &c., of electrolytes, metals, and amalgams ; the degree of "dissociation" of electrolytes, &c.

Nearly all the substances employed were of a high degree of purity, and all the electrolytic ones were taken in the proportions of their chemical equivalent weights. Nearly all the solutions, whatever their diluent, formed chemically equivalent volumes. In consequence of the strong voltaic action of the halogens with the positive metal, the degree of strength of their solutions (except that of bromine in Experiment 4) was 1 equivalent weight in grains in 528,550 grains of water, whilst that of all the acids, salts, and alkalies was 1 such equivalent in 1,800 grains of water. The total volume of liquid used in each experiment with the halogens was 10·0 cubic centims., but with the acids, salts, and alkalies it was 6·0 c.c. ; the volume of water used for dilution was in all cases *four times* that of the dissolved electrolyte. Distilled water was employed in making and diluting all the solutions. All the measurements of electromotive force were made at ordinary

atmospheric temperatures ; the latter are omitted for the sake of brevity. In every instance with electrolytes, each electromotive force represents a difference between the *mean* electromotive force of the metal and liquid at the positive plate, and a similar counter one at the negative plate of the voltaic couple ; the negative plate being in nearly all cases composed of platinum, this opposing force was usually small. All cases in which the electromotive force was very variable are mentioned ; the least uniform results occurred with solution of potassium cyanide and with caustic potash ; the results obtained with an amalgam of magnesium were usually inaccurate, and the amalgam, by very brief exposure to the air, acquired a film of black suboxide of magnesium. As water excites an electromotive force with each voltaic couple, its influence has to be considered and taken into account in every case of its addition to the electrolyte. In all cases of such addition, not only is the more active substance diluted by the water, but also the water by that substance ; the proportion of the latter substance to water being however very small, its influence as a diluent is equally small and has not been considered. Care was taken to employ diluents which did not chemically combine with the substance to be diluted, any exceptions to this are mentioned.

The results will be more clearly understood if we carefully distinguish between several phenomena, viz.:—First, the production of a direct electromotive force at the positive plate, increasing the current ; second, of that of an inverse electromotive force at the negative plate, decreasing or in some cases reversing the current ; and third, the loss of mean electromotive force when chemical union has occurred between the constituents of the liquid, or between the two metals of an alloy when used as a positive plate.

The research is divided into six sections, viz. :—*A*, Influence of Dilution of the Electrolyte, using different halogens, acids, salts, and alkalies, and showing the rate of variation of *mean* amount of electromotive force caused by the dilution ; and the influence of chemical union and substitution, of varying

the kind of negative metal, of the kind of solvent, and of temperature, upon the amount of effect of dilution. *B*, Influence of Dilution of the Electrolyte, using different positive metals, negative metals, and electrolytes; effects of dilution at one metal only upon the actual and mean amount of electromotive force, and the influence of viscosity of the electrolyte upon the effects of dilution. *C*, Influence of Liquefaction of the Positive Metal by means of mercury, using different positive metals, negative ones, and electrolytes. *D*, Influence of Dilution of the Positive Amalgam, using different amalgams, electrolytes, and negative metals, and showing the rate of variation of *mean* amount of electromotive force caused by the dilution. *E*, Influence of Liquefaction of the Negative Metal and of dilution of its amalgams; and, *F*, Influence of Diluting one Solid Metal by means of another; relation of volta-electromotive force to equivalent volumes of elementary substances, &c., &c.

The following tables of Section A show the actual and calculated amounts of electromotive force, and the simple and percentage amounts of variation of mean electromotive force from the calculated one, as caused by the dilution.

SECTION A.

Influence of Dilution of the Electrolyte; with Different Electrolytes.

TABLE 1.—*Solutions of Halogens.*   With Zn + Pt.

No of Expt.	Grains of Water.	Grains of Cl.	E. M. F. Volts.	E. M. F. of Mixture.	Calculated Mean E. M. F.	Change of Mean E. M. F.	Per cent.
1.	155 620	+ ·0107	1·9279 } 1·1270 }	1·7991	1·8000	Gain ·4991 =	88·39
2.	155 620	Br. + ·0241	1·8763 } 1·1270 }	1·6182	1·2742	Gain ·8890 =	26·64
3.	155 620	I. + ·0384	1·4416 } 1·1270 }	1·4215	1·1900	Gain ·2315 =	19·45

In the undiluted liquid of Experiment 2, one volume of bromine vapour was dissolved in 48·8 volumes of water, and in the diluted solution, one in 175·4 volumes.

These results show, first, that in each case dilution largely increased the *mean* amount of electromotive force; second, that the increase varied inversely as the atomic weights of the halogens; and third, that the more strongly electronegative the active ingredient of the electrolyte, the larger was the gain of *mean* amount of electromotive force by dilution.

When water is added to an aqueous solution of a halogen, the greater electronegative energy of the latter is diluted by the less electronegative energy of the former, and this tends to reduce the amount of electromotive force excited by the mixture and the positive metal; but, at the same time, the degree of freedom of the molecules of the far more energetic halogen is increased by the molecules being diffused in a larger bulk of the comparatively neutral water, and as the weight of water is vastly greater than that of the chlorine, the influence of the second circumstance more than counterbalances that of the first one. In this kind of case, at 16° centigrade, and in the absence of light, very little chemical union of the halogen with the elements of the water occurs to diminish the freedom of motion of its molecules; if, however, in the case of chlorine, the mixture is exposed to light, and especially if it is heated, the energy of union of the chlorine with the positive metal and the increase of *mean* amount of electromotive force by dilution are greatly diminished. In nearly all cases where chemical union occurs between the ingredients of the two liquids which are added together, the amount of electromotive force and of gain of *mean* amount of that force are diminished. (See Phil. Mag., *ibid.*)

In the next two experiments a solution of bromine was used of nearly 800 times the above strength and of the same degree of concentration as that of the acids, salts, and alkalies subsequently employed, in order to ascertain the degree of effect of a very strong solution in relation to that of a weak one, and to subsequently compare the effects with those obtained with the corresponding halogen acids, and their salts of the same degree of concentration. It must be observed that two different positive metals were used.

TABLE 2.—*Solutions of Halogens.*

No. of Expt.	Grains of Water.	Grains of Cl.	E.M.F. Volts. Pt.	E.M.F. of Mixture.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
4.	Br with Zn +						
	18 72	+ ·80	1·9878} 1·1270}	1·9792	1·8026	Gain ·6766 =	52·04
5.	Br with Cd + Pt.						
	18 72	+ ·80	1·5707} ·85	1·5621	·9970	Gain ·5651 =	56·68

Each solution may be viewed as one of mixed liquid and vaporous bromine.

Owing to the energetic action of the solutions upon the positive metal, the measurements of electromotive force were slightly irregular. The numbers given by Experiment 4 when compared with those of Experiment 2 show that by increasing the degree of concentration of the solution 282·1 times, the percentage of gain was barely doubled.

In order to ascertain the effect of a series of equal dilutions, a solution of chlorine was diluted by the addition of nineteen successive and equal quantities of water, and the electromotive force measured by means of a zinc and platinum couple, and its mean amount calculated after each addition. The initial solution was slightly weaker than that used in Experiment 1 and contained 1 equivalent weight of chlorine in grains in 550,250 grains of water, or ·01 grain in 155 grains of water; the electromotive force of that solution was used as the basis of calculation throughout the series. The following are the results:—

Rate of Variation of Mean Amount of Electromotive Force by Dilution of the Electrolyte.

Experiment 6. Table 3.—*Chlorine Water.* With Zn+Pt.

Grains of Cl.	E.M.F. of Mixture.	Calculated Mean E.F.M.	Change of Mean E.M.F. Per cent.	
·0100	1·935			
·0095	1·980	1·8936	Gain ·0864 =	4·56
·0090	,,	1·8851	,, ·1249 =	6·73
·0085	1·995	1·8140	,, ·1810 =	9·97
·0080	,,	1·7735	,, ·2215 =	12·49
·0075	1·980	1·7355	,, ·2445 =	14·09
·0070	1·900	1·6921	,, ·2079 =	12·28
·0065	1·890	1·6559	,, ·2341 =	14·13
·0060	1·865	1·6124	,, ·2526 =	15·68
·0055	,,	1·5758	,, ·2892 =	18·36
·0050	1·840	1·5310	,, ·3090 =	20·19
·0045	,,	1·4910	,, ·3490 =	23·42
·0040	1·827	1·4506	,, ·3764 =	25·95
·0035	1·838	1·4108	,, ·4277 =	30·33
·0030	1·808	1·3697	,, ·4383 =	31·99
·0025	1·780	1·3290	,, ·4510 =	33·93
·0020	1·775	1·2886	,, ·4864 =	37·76
·0015	1·778	1·2483	,, ·5297 =	42·44
·0010	1·775	1·2078	,, ·5672 =	46·99

According to these results, each dilution except the sixth produced an increase of *mean* amount of electromotive force ; the proportion of gain by the first dilution and the last one was in each case 4·55 per cent., but the magnitudes of the other increases were somewhat variable.   The line which graphically represents the calculated *mean* amounts of electromotive force is necessarily a straight one, because all the additions of water were equal ; and the one which represents the percentage series of gains, although irregular in form, intersects a straight one in several places throughout, as if the amount of effect of each dilution was substantially the same, but was affected by small irregularities in the experimental measurements or by other causes.   Whilst the simple and calculated electromotive forces decreased throughout the series, the *gain* of mean electromotive force increased.

The entire amount of water added in the nineteen dilutions influenced the results in two ways, viz. :—First, the water, by being a weaker liquid, decreased the *mean* electromotive force ·22 volt ; and second, by permitting greater freedom of motion of the molecules of chlorine, it increased the simple electromotive force ·686 volt, thus leaving a balance of increase of mean electromotive force amounting to ·466 volt or 46·99 per cent.

As the *mean* amounts of electromotive force and the form of curve yielded by diluting the electrolyte are liable to be affected by any chemical action upon the negative metal, a series of similar measurements were now made with the same voltaic couple, but employing dilute hydrochloric acid instead of chlorine water.

Experiment 7. Table 4.—*Solution of HCl.*

Grains of HCl.	E.M.F. or Mixture.	Calculated Mean E.M.F.	Change of Mean E.M.F. Per cent.	
·01	1·355			
·0095	,,	1·3444	Gain ·0106=	·79
·009	1·342	1·3324	,, ·0096=	·72
·0085	,,	1·3208	,, ·0212=	1·60
·008	1·345	1·3097	,, ·0353=	2·69
·0075	1·340	1·2980	,, ·042 =	3·23
·007	,,	1·2867	,, ·0533=	4·14
·0065	,,	1·2760	,, ·0640=	5·01
·006	1·328	1·2645	,, ·0635=	5·02
·0055	1·308	1·2530	,, ·0435=	3·47
·005	1·295	1·2410	,, ·054 =	4·35
·0045	,,	1·2280	,, ·067 =	5·45
·004	,,	1·2178	,, ·0772=	6·32
·0035	,,	1·2070	,, ·088 =	7·29
·003	1·295	1·1950	,, ·100 =	8·36
·0025	1·290	1·1842	,, ·106 =	8·95
·002	,,	1·1725	,, ·1172=	10·0
·0015	1·275	1·1600	,, ·1150=	9·91
·001	,,	1·1498	,, ·1250=	10·86

The general form of the curve representing these percentages numbers is not widely different from that yielded by chlorine water; the total change was, however, only 10·86 instead of 46·99 per cent. as in the previous table, in consequence of the energy of the chlorine being reduced by its union with hydrogen. The irregularities in the forms of the curves yielded by chlorine and hydrochloric acid did not appear to be entirely due to slight variations in the manipulation, but partly to the properties of those substances.

As in these two series of dilutions the mean amount of electromotive force increased substantially, though irregularly, at the same rate as the dilution, the water added did not chemically unite with the dissolved substances.

In nearly all the following experiments of this section the voltaic couple was composed of cadmium and platinum; any exceptions to this are indicated.

TABLE 5.—*Solutions of Acids.* With Cd + Pt.

No. of Expt.	Electrolyte.	Grains of Grs. Water.	E.M.F.	Grains of Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
	H²O		·850					
8.	HCl	·365+18·	1·1217	+72	1·07082	·9048	Gain ·1654 =	18·26
9.	HBr	·810+18·	1·11026	+72	1·0645	·9082	,, ·1618 =	17·86
10.	HI	1·280+18·	1·0981	+72	1·0216	·9004	,, ·1212 =	18·46

Dilution increased the *mean* amount of electromotive force, &c., in each case, and the increases were very much smaller than those produced by equal proportions of dilution of each of the corresponding halogens in Tables 1, 2, and 8, notwithstanding that the acid solutions were about three hundred times more concentrated than the halogen ones. The increases varied in magnitude inversely as the molecular weights of the acids, and the strongest acid gave the greatest electromotive force and the largest percentage gain of *mean* amount of that force by dilution.

INFLUENCE OF CHEMICAL UNION UPON THE AMOUNT OF EFFECT OF DILUTION.

By comparing the effects in Experiment 9 with those obtained by means of an equally concentrated molecular weight solution of bromine in Experiment 5, we find that by the chemical union of hydrogen with the bromine, the percentage of gain of *mean* amount of electromotive force by dilution was reduced from 56·68 to 17·86. The same influence reduced the simple electromotive force of the undiluted solution of bromine from 1·5707 to 1·11026; that of the diluted one from 1·5021 to 1·0845, and the calculated mean amount of that of the diluted one from ·9070 to ·9082. (See also remarks at the end of Table 4.) The influence of chemical union of the ingredients of two liquids with each other upon the *mean* amount of electromotive force excited by the two substances has already been investigated in a research on "A Method of Measuring Loss of Energy Due to Chemical Union," &c. (See Phil. Mag., January, 1862, p. 28.)

TABLE 6.—*Solutions of Acids*, continued.

No. of Expt.	Electrolyte	Grains of Grm.	Grains of Water	E.M.F.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
11.	H^{2}SO^4	·40 +1x	1·1046 +7x	1·1860	·0187	Gain ·2228		24·82
12.	HNO^3	·68 +1x	1·18314+7x	1·11026	·0078	·2020		28·80
13.	H^{2}C^{2}O^4	·80 +1x	1·19320+7x	1·1274	·0106	·2078		22·58
14.	HClO^3	·445+1x	1·0045 +7x	1·0210	·0080	·1277		14·28
15.	Citric acid	·64 +1x	1·08108+7x	1·0218	·0008	·1801		15·51
16.	HIO^3	1·78 +1x	1·0850 +7x	·9080	·0002	·1088		11·07
17.	Oxalic acid	·45 +1x	1·0508 +7x	·9080	·0008	·1027		11·58
18.	Formic	·40 +1x	·7808 +7x	·8720	·2970	·0050		7·06

The proportions of water employed were the same as in Experiments 8, 9, and 10. Similar results have already been obtained with tartaric and acetic acid by means of the same voltaic couple, the gains being 21·0 and 7·06 per cent. respectively. (See Phil. Mag., August, 1861, pp. 158-65.)

TABLE 5.—*Solutions of Acids.* With Cd + Pt.

No. of Expt.	Electro-lyte. H^2O	Grains of Grs. Water.	Grains of E.M.F. Water. ·850	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
8.	HCl	·865+18·	1·1217 +72	1·07082	·9048	Gain ·1654 =	18·26
9.	HBr	·810+18·	1·11026+72	1·0645	·9032	,, ·1618 =	17·86
10.	HI	1·280+18·	1·0981 +72	1·0216	·9004	,, ·1212 =	13·46

Dilution increased the *mean* amount of electromotive force, &c., in each case, and the increases were very much smaller than those produced by equal proportions of dilution of each of the corresponding halogens in Tables 1, 2, and 8, notwithstanding that the acid solutions were about three hundred times more concen-trated than the halogen ones. The increases varied in magnitude inversely as the molecular weights of the acids, and the strongest acid gave the greatest electromotive force and the largest percentage gain of *mean* amount of that force by dilution.

INFLUENCE OF CHEMICAL UNION UPON THE AMOUNT OF EFFECT OF DILUTION.

By comparing the effects in Experiment 9 with those obtained by means of an equally concentrated molecular weight solution of bromine in Experiment 5, we find that by the chemical union of hydrogen with the bromine, the percentage of gain of *mean* amount of electromotive force by dilution was reduced from 56·68 to 17·86. The same influence reduced the simple electromotive force of the undiluted solution of bromine from 1·5707 to 1·11026; that of the diluted one from 1·5621 to 1·0645, and the calculated *mean* amount of that of the diluted one from ·9970 to ·9082. (See also remarks at the end of Table 4.) The influence of chemical union of the ingredients of two liquids with each other upon the *mean* amount of electromotive force excited by the two substances has already been investigated in a research on "A Method of Measuring Loss of Energy Due to Chemical Union," &c. (See Phil. Mag., January, 1892, p. 28.)

TABLE 6.—*Solutions of Acids*, continued.

No. of Expt.	Electrolyte.	Grains of Water. Grs.	Water.	E.M.F.	Grains of Water. Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
11.	H^2SO^4	·49	+18	1·1646	+72	1·1360	·9187	Gain ·2228	=	24·82
12.	HNO^3	·63	+18	1·13814	+72	1·11026	·9073	,, ·2029	=	28·36
13.	H^2CrO^4	·59	+18	1·19820	+72	1·1274	·9196	,, ·2078	=	22·58
14.	$HClO^3$	·845	+18	1·0645	+72	1·0216	·8939	,, ·1277	=	14·28
15.	Citric acid	·64	+18	1·08166	+72	1·0216	·8968	,, ·1391	=	15·51
16.	HIO^3	1·76	+18	1·0859	+72	·9980	·8892	,, ·1038	=	11·67
17.	Oxalic acid	·45	+18	1·0502	+72	·9980	·8903	,, ·1027	=	11·53
18.	Formic ,,	·46	+18	·7356	+72	·8729	·8270	,, ·0659	=	7·96

The proportions of water employed were the same as in Experiments 8, 9, and 10.

Dilution increased the *mean* amount of electromotive force in every case. Similar results have already been obtained with tartaric and acetic acid by means of the same voltaic couple, the gains being 21·0 and 7·06 per cent. respectively. (See Phil. Mag., August, 1891, pp. 158-65.)

TABLE 7.—*Solutions of Acid Salts.*

No. of Expt.	Electrolyte	Grs. Water.	E.M.F.	Grains of Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
19.	AmAlum	·593+18	1·0645	·598+72	1·0278	·8988	Gain ·1385	=	14·94
20.	KHSO⁴	·68 +18	1·10168	+72	1·0359	·9014	,, ·1345	=	14·92
21.	BeSO⁴	·526+18	1·0502	+72	·9987	·8908	,, ·1079	=	12·11

Dilution increased the *mean* amount of electromotive force in each case; the percentages of increase were smaller than those obtained with the strong acids; but larger than those given by the weak ones.

TABLE 8.—*Solutions of Neutral Salts.*

No. of Expt.	Electrolyte	Grs. Water.	E.M.F.	Grains of Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
22.	Cs²SO⁴	1·81 +18	·9873	+72	·9472	·8790	Gain ·0652	=	7·75
23.	KCl	·745+18	·9844	+72	·9415	·8774	,, ·0641	=	7·80
24.	NaCl	·585+18	·9958	+72	,,	·8797	,, ·0618	=	7·02
25.	MgSO⁴	·600+18	·9787	+72	·9358	·8765	,, ·0598	=	6·76
26.	LCl	·425+18	,,	+72	·9787	·8759	,, ·0570	=	6·50
27.	ZnSO⁴	·805+18	,,	+72	·9829	·8766	,, ·0563	=	6·42
28.	CdSO⁴	1·04 +18	·9701	+72	·9272	·8749	,, ·0523	=	5·97
29.	Rb²SO⁴	1·38 +18	·9472	+72	·9186	·8705	,, ·0481	=	5·52
30.	BaCl²	1·04 +18	·97298	+72	·9243	·8777	,, ·0466	=	5·31
31.	SrCl²	·79 +18	·9644	+72	·9058	·8755	,, ·0408	=	4·60
32.	CsCl	1·68 +18	·9386	+72	·9072	·8689	,, ·0383	=	4·40
33.	RbCl	1·20 +18	·9329	+72	·90148	·8674	,, ·0340	=	3·92
34.	CaCl²	·555+18	·9538	+72	·9043	·8726	,, ·0317	=	3·68

With this series of substances also, each gave an increase of *mean* electromotive force by dilution. The entire series gave an average percentage gain of only one 2·5th part of that given by the group of acid salts, and one 2·9th part of that given by the series of acids, thus showing that the effects of dilution usually diminished with the simple electromotive force and with the energy of chemical action of the liquid upon the positive metal. The halogen salts of caesium, rubidium, and calcium gave the least electromotive force and the smallest percentage of gain, probably because the halogens were strongly chemically united to the alkalies, and, therefore, had less action upon the cadmium positive metal.

With regard to any numerical relation of such gain to the equivalent weights of the salts and of their metallic bases, with the magnesium group, the percentage of gain varied inversely as those weights ; with the barium group it varied directly ; with the group composed of potassium, sodium, and lithium, and with the one formed of rubidium and caesium it also varied directly. The proportion of gain was evidently related in a general way to those weights, and in each group it was largest with the most energetic and most electropositive metal. The relation of the proportion of gain to the equivalent weight of the electronegative constituent of the salt was similarly examined, and is shown by the numbers in the following table :—

TABLE 9.—*Solutions of Neutral Salts.*

No. of Expt.	Electro- lyte.	Grains of Grs. Water.	Grains of E.M.F Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
85.	KBr	1·19+18	·8951+72	·8986	·8595	Gain ·0391	=	4·54
86.	KI	1·66+18	·8814+72	·8357	·8566	Loss ·0209	=	2·44

On comparing the percentage gains in these two cases with that given by KCl in Table 8, the three are found to constitute a series, in which the gains vary in magnitude directly as the molecular weights of the salts, as they did of the corresponding acids in Experiments 8, 9, and 10, and of the halogens themselves in Experiments 1, 2, and 3.

On comparing the numbers in Experiment 5 with those in Experiment 85, we find that by the chemical union of potassium with bromine in a solution of the same degree of concentration, the percentage gain of *mean* amount of electromotive force by equal dilution of an equivalent solution of bromine was reduced from 56·68 to 4·54, and by comparing them with those in Experiment 9 it is further shown that by the substitution of potassium for hydrogen in aqueous hydrobromic acid, the percentage of such gain was diminished from 17·86 to 4·54.

TABLE 10.—*Solutions of Alkaline Salts.*

No. of Expt.	Electro-lyte.	Grs. Water.	E.M.F.	Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
87.	NaHCO³	·42 +18	·8214	+72	·8271	·8441	Loss ·017	=	2·01
88.	KHCO³	·50 +18	·8156	+72	·8214	·8430	,, ·0216	=	2·56
89.	KCy	·65 +18	·7899	+72	·8156	·8877	,, ·0221	=	2·63
40.	Na³HPO⁴	·478+18	·8357	+72	·8214	·8472	,, ·0258	=	3·04
41.	Na²CO³	·53 +18	·7585	+72	·7899	·8312	,, ·0412	=	4·97
42.	K²CO³	·69 +18	·7899	+72	·7899	·8376	,, .0477	=	5·69

The cyanide of potassium contained 92·11 per cent. of the actual substance.

In each of these cases, as the actual electromotive force of the mixture was less than that given by water, viz., ·85 volt, the changes of *mean* amount of that force were all losses. The losses were usually larger in proportion as the salts were more alkaline; the reduction of acid carbonate to monocarbonate by removal of half the carbonic acid was attended by about the same amount of increase of loss, viz., 3·0 per cent. in the case of the salt of sodium, as in that of potassium; this further shows that the acid constituent of the salt exercises a large influence upon the proportion of gain or loss. The probable reason why the liquids excited less electromotive force than water, and produced losses, was that they acted chemically more strongly than water upon the platinum plate in comparison with that upon the cadmium one, and thus produced a larger degree of counter electromotive force.

It is well known that a solution of potash has more chemical action upon platinum than upon silver; in order, therefore, to ascertain whether the losses were due to such action upon the negative plate, the measurements were repeated with a cadmium silver voltaic couple. The following are the results:—

TABLE 11.—*Solutions of Alkaline Salts,* Cd + Ag.

No. of Expt.	Electro- lyte.	Grains of Grs. Water.	Grains of Water E.M.F.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	H²O			·7642				
43.	KHCO³	·50 +18	·8500+72	·8442	·7816	Gain ·0626	=	8,0
44.	NaHCO³	·42 +18	·8500+72	·8442	·7816	,, ·0541	=	6·92
45.	Na²HPO⁴	·478+18	·8857+72	·8214	·7787	,, ·0427	=	5·48
46.	K²CO³	·69 +18	·7928+72	·7871	·7661	,, ·0210	=	2·74
47.	Na²CO³	·53 +18	·7599+72	·7814	·7694	,, ·0120	=	1·55
48.	KCy	·65 +18	·5040+72	·5068	·7111	Loss ·2043	=	28·7

The conversion of nearly all the losses of Table 10 into gains, and the large increase of loss of *mean* amount of electromotive force with the solution of potassium cyanide in this table, were due to the employment of a silver negative plate instead of a platinum one, silver being usually less acted upon chemically than platinum by solutions of other alkaline salts, and more so than platinum by one of potassium cyanide ; the counter electromotive force, therefore, in the experiments of Table 11 was greater with potassium cyanide and less with all the other salts than in Table 10.

TABLE 12.—Solutions of Alkalies, Cd + Pt.

The caustic soda was made from metallic sodium and was highly pure; the potash contained 2·85 per cent. of carbonate; and the rubidia and caesia were freshly made from their pure sulphates by means of hydrate of barium.

No. of Expt.	Electrolyte. H²O	Grs.	Grains of Water	E.M.F.	Grains of Water	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	H²O			·8500						
49.	RbHO	1·02	+ 18	·8843	+ 72	·8214	·8571	Loss ·0357	=	4·16
50.	KHO	·56	+ 18	·8843	+ 72	·8214	·8572	,, ·0358	=	4·17
51.	CsHO	1·50	+ 18	·8900	+ 72	·8214	·8584	,, ·0370	=	4·81
52.	NaHO	·40	+ 18	·8786	+ 72	·8185	·8557	,, ·0372	=	4·84

In this group of instances the amount of simple electromotive force excited by water alone was slightly less than that excited by each of the undiluted alkaline solutions; this circumstance, together with the much larger weight of the water than of either of those liquids, the almost entire absence of any acid in the electrolyte to act upon the positive metal, and the chemical action of the alkali upon the platinum, were together sufficient to account for the *loss* of *mean* amount of electromotive force in each case.

The results obtained by using silver instead of platinum as the negative plate with alkalies are given in the next table.

TABLE 13.—*Solutions of the Alkalies,* Cd+Ag.

No. of Expt.	Electrolyte.	Grains of Grs. Water.	E.M.F. Water.	Grains of Water.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
	H²O		·7642					
53.	KHO	·56+18	·8500 + 72		·8357	·7817	Gain ·0540 =	6·90
54.	NaHO	·40+18	·8528 + 72		·8357	·7822	„ ·0535 =	6·88

These results show that the losses in Table 12 were due to the greater counter electromotive force produced by the action of the alkali upon the platinum negative plate than upon a silver one.

Influence of the kind of Solvent.

Two experiments were made with a cadmium platinum couple, using as a solvent and diluent a mixture of equal volumes of water and absolute alcohol instead of water alone ; the following are the results :—

TABLE 14.

No. of Expt.	Electrolyte.	Grains of Grs. Sp.Vin.	Sp.Vin. E.M.F.	Grains of Sp.Vin.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
	Sp.Vin		·8643					
55.	LCl	·425+17	·9858 + 68		·9858	·8792	Gain ·0566 =	6·43
56.	CaCl²	·555+17	·9472 + 68		·9472	·8815	„ ·0657 =	7·45

On comparing these results with those of Nos. 26 and 84, it will be seen that whilst the *mean* electromotive force was slightly decreased with LCl it was doubled with CaCl². Change of kind of solvent did not prevent the increase of *mean* electromotive force on dilution.

Influence of Temperature of the Electrolyte.

In these Experiments the mixtures employed were the same as in Nos. 8 and 28, and the same voltaic couple of Cd+Pt was used, the only difference being that in the former instances the temperature of the liquids was that of the atmosphere, about 16°C., whilst in the present ones it was 80°C.

TABLE 15.

No. of Expt.	Electrolyte.	Grains of Grs. Water. E.M.F.	Grains of Water. E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	H²O	·8500					
57.	HCl	·865+18 1·1217	+ 72 1·0788	·7048	Gain ·1740	=	19·2
58.	KCl	·745+18 ·9844	+ 72 ·9358	·8774	,, ·0584	=	6·65

The gain of *mean* electromotive force of the HCl was a little increased, and that of KCl was a little decreased. As the alterations of volume due to increase of temperature were very small in comparison with those due to dilution, the effects upon the gain of electromotive force were not expected to be large. Rise of temperature did not prevent the increase of *mean* electromotive force on dilution.

REMARKS ON SECTION A.

The results show:—First, that the amount of change of *mean* electromotive force of the voltaic couple by dilution varied with the kind of electrolyte; with a zinc platinum or cadmium platinum couple, all the halogens, acids, acid salts, and neutral ones gave "gains," and all the alkaline ones and the alkalies gave "losses;" and the magnitudes of the "gains" were greatest with the halogens, less with acids and acid salts, and least with neutral salts; with the halogens and their acids it was greater the smaller their molecular weight and the larger their chemical energy; with the neutral salts it was largely affected by their negative and slightly by their positive ingredient; second, it varied with the kind of negative

metal; by employing one which was less acted upon by alkalies, viz., silver instead of platinum, nearly all the "losses" which occurred with alkaline salts and the alkalies were converted into "gains" and the remaining ones were greatly reduced in magnitude; and third, the electronegative constituent of the electrolyte had far greater influence than the electropositive one upon the amount of change of electromotive force produced by dilution. A different kind of solvent or a higher temperature of the electrolyte had no great effect on the particular cases examined.

The whole of the results of the experiments in this section agree with the conclusion that, *dilution of an electrolyte increased the electromotive force and chemical energy of the substance diluted, and that this increase was due to greater freedom of motion of the molecules of the diluted substance.* First, the results given in Tables 3 and 4 show that *the gain of mean amount of electromotive force varied directly and substantially, though irregularly, at the same rate as the dilution*, and as the molecular distance of the electronegative ingredient of the electrolyte; second, by diluting the electrolyte of a simple voltaic cell with water the *mean* amount of electromotive force and chemical action of the active dissolved substance both at the positive and negative plates was increased, and this increase was due to increase of molecular energy of the substance which unites with the metals and not of that of the water; third, if by diluting the electrolyte the energy of action increased faster at the positive plate than at the negative one, there was a "gain" of *mean* amount of electromotive force of the resulting current, but if it increased faster at the negative plate there was a "loss;" and fourth, the amount of variation of *mean* electromotive force of the current was determined, not by the change of electromotive force at the positive plate or the negative one alone, but by the *difference* of the two.

SECTION B.

INFLUENCE OF DILUTION OF THE ELECTROLYTE, USING DIFFERENT POSITIVE METALS.

In each table of this section the kind of positive metal was varied, and that of the electrolyte was kept constant. In the cases of potassium and sodium it was necessary to employ their amalgams, each amalgam was composed of 1 equivalent of the metal in grains dissolved in sufficient mercury to form a total of 5,600 grains. The negative metal in all the experiments in this section, except those of Table 21 and Experiments 108 and 110, was platinum.

TABLE 16.—*Solution of ·365 grains HCl.* Neg. metal Pt.

No. of Expt.	Positive Metal.	Grains of Water.	E.M.F.	Grains of Water.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
59.	Ag	18	·0286+HCl	·2574+72	·2845	·0746	Gain ·1599	=	214·8
60.	Ni	18	·2059+HCl	·6849+72	·5884	·2923	,, ·2911	=	99·5
61.	Sb	18	·2431+HCl	·4719+72	·4483	·2891	,, ·1542	=	53·8
62.	Tl	18	·5720+HCl	·8866+72	·8522	·6353	,, ·2169	=	84·1
63.	In	18	·5948+HCl	·9009+72	·8580	·6574	,, ·2016	=	30·7
64.	Mg	18	1·4700+HCl	1·7844+72	1·9419	1·5333	,, ·4086	=	26·6
65.	Zn	18	1·1270+HCl	1·4678+72	1·4244	1·1955	,, ·2289	=	19·3
66.	Al	18	·8880+HCl	1·1297+72	1·0489	·8967	,, ·1472	=	16·4
67.	Sn	18	·6850+HCl	·8066+72	·7579	·6695	,, ·0884	=	13·2
68.	Te	18	·1880+HCl	·2280+72	·2195	·1910	,, ·0285	=	12·3
69.	Si	18	·2516+HCl	·3482+72	·3003	·2700	,, ·0303	=	11·2
70.	K+Hg	18	2·8092+HCl	2·5950+72	2·5666	2·8667	,, ·1999	=	8·44
71.	Pb	18	·6650+HCl	·7978+72	·7099	·6574	,, ·0506	=	7·66
72.	Na+Hg	18	2·2006+HCl	2·4580+72	2·4008	2·2524	,, ·1484	=	6·58

Table 17.—*Solution of ·65 grain KCy (92·11 per cent.).*

No. of Expt.	Positive Metal	Grains of Water	E.M.F.	E.M.F. Water	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
73.	Ag	18	·0286 +KCy	·2574+72	·2481	·0752	Gain ·1679	=	228·2
74.	Pd	18	·0 +KCy	·5205+72	·3146	·1062	„ ·2084	=	196·2
75.	Hg	18	·08294+KCy	·5863+72	·3718	·1856	„ ·1862	=	100·3
76.	Cu	18	·2602 +KCy	·8322+72	·6892	·8750	„ ·8142	=	83·78
77.	Sb	18	·2481 +KCy	·5005+72	·4576	·2957	„ ·1619	=	54·75
78.	Al	18	·8380 +KCy	1·6958+72	1·4529	·9926	„ ·4608	=	46·87
79.	Bi	18	·2860 +KCy	·4862+72	·4576	·8268	„ ·1808	=	40·01
80.	Ni	18	·2059 +KCy	·2691+72	·2345	·2176	„ ·0169	=	7·76
81.	Fe	18	·5662 +KCy	·5876+72	·5434	·5603	Loss ·0169	=	3·01
82.	Mg	18	1·4700 +KCy	1·1840+72	1·1840	1·4115	„ ·2275	=	16·12

The position of silver and palladium in the series indicates the strong chemical action of the liquid upon them. The results in No. 74 were variable and in No. 75 very variable. Cyanide of potassium solutions yielded less uniform results than any other electrolyte.

Table 18.—*Solution of 1·28 grains HI.*

83.	Ag	18	·0286+HI	·0868+72	·0629	·0406	Gain ·0223	=	54·9

Table 19.—*Solution of ·56 grain KHO.* Negative metal Fe.

84.	Sb	18	–·8146+KHO	·4818+72	·4175	–·1618	Gain ·5798	=	–858·0
85.	Al	18	·286+KHO	1·0480+72	1·0010	·4187	„ ·5823	=	189·04

TABLE 20.—Solution of ·56 grain KHO. Negative metal Pt.

No. of Expt.	Positive Metal.	Grains of Water.	E.M.F.	Grains of Water E.M.F. Water +72	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
86.	Te	18	·1890+KHO	·4147+72	·4004	·2304	Gain ·1700	=	73·78
87.	Sb	18	·2481+KHO	·5005+72	·4083	·2957	„ ·1476	=	49·40
88.	Al	18	·8380+KHO	1·8814+72	1·8528	·9491	„ ·4087	=	42·58
89.	Sn	18	·6850+KHO	·9210+72	·8852	·6985	„ ·1417	=	20·43
90.	Pb	18	·6635+KHO	·8065+72	·7521	·6928	„ ·0598	=	8·56
91.	In	18	·5948+KHO	·6578+72	·6292	·6076	„ ·0216	=	6·07
92.	Si	18	·2516+KHO	·2873+72	·2516	·2486	„ ·008	=	1·20
93.	Tl	18	·5720+KHO	·5484+72	·5491	·5660	Loss ·0169	=	2·9
94.	Cd	18	·8500+KHO	·8843+72	·8214	·8572	„ ·0858	=	4·17
95.	Zn	18	1·1270+KHO	1·2185+72	1·0469	1·1457	„ ·0988	=	8·62
96.	Na+Hg	18	2·2006+KHO	1·7659+72	1·8860	2·1116	„ ·2256	=	10·69
97.	K+Hg	18	1·2292+KHO	1·7716+72	1·8682	2·1355	„ ·2723	=	12·78
98.	Mg	18	1·4700+KHO	1·4928+72	1·2698	1·4746	„ ·2048	=	13·88
99.	Ni	18	·2059+KHO	·0629+72	·1058	·1766	„ ·0708	=	40·08

The caustic potash contained 2·85 per cent. of K^2CO^3. Probably in the presence of potash, metallic tellurium and antimony decompose water and form acids which unite with the potash to constitute salts.

The metals which yielded losses of mean electromotive force in Table 20 were now examined by the aid of a cadmium silver voltaic couple; the following are the results :—

TABLE 21.—*Solution of ·56 grain KHO. Negative metal Ag.*

No. of Expt.	Positive Metal.	Grains of Water.	E.M.F.	Grains of E.M.F. Water.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
100.	Sn	18	·2331+KHO	·2860+72	·2574	·2359	Gain ·0215	=	9·11
101.	Ni	18	·1859+KHO	·2574+72	·2145	·2005	,, ·0140	=	7·00
102.	Tl	18	·5720+KHO	·6849+72	·6234	·5848	,, ·0386	=	6·60
103.	Na+Hg	18	2·1577+KHO	2·1291+72	2·1291	2·1518	,, ·0227	=	1·05
104.	K+Hg	18	2·1868+KHO	2·1684+72	2·1684	2·1816	Loss ·0182	=	·88
105.	Zn	18	1·0698+KHO	1·1270+72	1·0412	1·0815	,, ·0408	=	8·72
106.	Mg	18	1·4214+KHO	1·1983+72	1·2555	1·3754	,, ·1199	=	8·71

The effects with magnesium and zinc in the potash solution were slightly variable. Comparison of the results in this table with those in Table 20 shows that the losses in Table 20 were largely due to the use of a negative plate of platinum which was more acted upon than silver in the alkaline liquid.

In the next two tables the difference of effect with negative plates of platinum and silver in alkaline solutions is further shown.

TABLE 22.—*Solution of ·4 grain NaHO.*

No. of Expt.	Positive Metal.	Grains of Water.	E.M.F.	Grains of Water. E.M.F.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
107.	Cd+Pt	18	·8500+NaHO	·8786+72	·8185	·8557	Loss ·0872	=	4·84
108.	Cd+Ag	18	·7642+NaHO	·8528+72	·8857	·7882	Gain ·0585	=	6·88

TABLE 23.—*Solution of ·88 grain Borax.*

No. of Expt.	Positive Metal.	Grains of Water.	E.M.F.	Grains of Water. E.M.F.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
109.	Cd+Pt	18	·8500+Borax	·7642+72	·7642	·8327	Loss ·0685	=	8·22
110.	Cd+Ag	18	·7642+Borax	·7928+72	·7785	·7699	Gain ·0086	=	1·11

Owing to the insufficient solubility of this salt the proportion of it was reduced to one-third of the equivalent quantity.

In each of these two tables, the less corrosion of a plate of silver in alkaline solution gave less counter electromotive force and was attended by a gain instead of a loss.

Effect of Dilution of the Electrolyte at one metal only.

First—Upon the SIMPLE *Amount of Electromotive Force of the Couple.*

Some experiments were made to ascertain the effect upon the amount of *simple* electromotive force, of diluting the electrolyte at one metal only of the voltaic couple ; the solutions were of the usual degrees of strength. The liquids were separated by a diaphragm of clean parchment paper. A thick and shallow glass cup was divided vertically into two equal parts; the diaphragm, attached to a frame of sheet india-rubber, was placed between the two halves, and the whole held together tightly by a metal clamp screw. See Fig. 1. The following tables show the results :—

TABLE 24.—*Solution of* ·365 *grain HCl.*

No. of Expt.	Voltaic Couple.	Both metals in strong solution. E.M.F.	Both metals in diluted solution. E.M.F.	Positive metal only in strong solution. E.M.F.	Negative metal only in strong solution. E.M.F.
111.	Cd+Pt	1·1217	1·0702	1·1217	1·0589
112.	Ni+Pt	·6849	·5884	·7486	·7150
113.	Sb+Pt	·4719	·4576	·4919	·4576

TABLE 25.—*Solution of* ·49 *grain* H^2SO^4.

114.	Cd+Pt.	1·1646	1·1360	1·1646	1·1302

TABLE 26.—*Solution of* ·59 *grain* H^2CrO^4.

115.	Cd+Pt	1·1932	1·1274	1·2075	1·1360

TABLE 27.—*Solution of* ·56 *grain KHO.*

116.	Sb+Ag	·6864	·6849	·6864	·6849
117.	Sb+Pt	·6578	·6006	·6578	·6284

TABLE 28.—*Solution of* ·65 *grain KCy.*

118.	Ag+Fe	·2860	·2802	·2860	·2860
119.	Ag+Pt	·2574	·2481	·2574	·2481
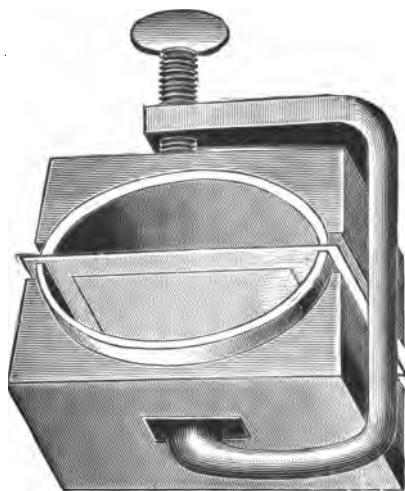
Fig. 1.

In these experiments, by diluting the electrolyte at the positive plate only, the *simple* electromotive force was diminished in seven cases, unaltered in one, and increased in one. By diluting it at the negative plate only, the simple electromotive force was increased in three cases, and unaffected in six. And in eight out of the nine instances, the simple electromotive force was larger, and in no case smaller, with the positive metal than with the negative one in the undiluted solution. These results show that the effect of dilution in diminishing the simple electromotive force was greater at the positive plate than at the negative one; this was probably due to the greater energy of action at the former than at the latter. The dilution probably also affects the amount of simple electromotive force to a small extent by altering the degree of electric conduction resistance of the liquid. In all the cases the simple electromotive force was less with both metals in the weak solution than in the strong one.

Second.—Upon the MEAN *Amount of Electromotive Force
of the Couple.*

Some experiments were now made to ascertain the amount
of difference of effect of dilution upon the *mean* amount of
electromotive force at the positive plate in comparison with
that at the negative one.   The experiments were made in
pairs ; in the first of each pair the electrolyte was diluted at
the positive plate only, and in the second at the negative one
only, the other plate in each experiment being in water, and
the two liquids separated by a partition of clean parchment
paper as in the previous series.   In making the first experiment
of each pair, the electromotive force of the two metals was
measured :—First, with both the metals immersed in water ;
second, with the positive one in the undiluted solution of the
halogen, acid, or salt, and the negative one in water ; and third,
with the positive one in the diluted solution, and the negative
one in water.   And in the second experiment of the pair,
similar measurements were made with the negative metal in
the solution of halogen, or acid, &c., and the positive one in
water.   In these experiments the electromotive force of the
metal which was in water alone was disregarded; because the
only change which was made during the measurements was in
the other liquid.   The following tables show the results :—

TABLE 29.—*Solution of Bromine.*

No. of Expt.	Voltaic Couple.	Grains of Water.	E.M.F. with Water.	Grains.	E.M.F. with Solution.	Grains of Water.	E.M.F. after Dilution.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
120.	Cd+Pt	18	·8500	+ Br ·80	1·8940	+ 72	1·8648	·9621	Gain ·4027	= 41·9
121.	Cd+Pt	18	·8500	+ Br ·80	·9858	+ 72	·9014	·8684	Gain ·088	= 8·7

Dilution largely increased the direct *mean* electromotive force at the positive plate.

In Experiment 120 the percentage of gain was probably reduced by a little bromine diffusing through the parchment paper diaphragm, acting upon the negative metal and producing counter electromotive force; in Experiment 121 a diaphragm of thin biscuit ware was used in order to prevent this.

TABLE 30.—*Solutions of Acids.*

No. of Expt.	Voltaic Couple.	Grains of Water.	E.M.F. with Water.	Grains.	E.M.F. with Solution.	Grains of Water.	E.M.F. after Dilution.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
122.	Cd+Pt	18	·8500	+HCl ·365	1·1217	+ 72	1·0788	·9048	Gain ·1740	= 19·2
123.	Cd+Pt	18	·8500	+HCl ·365	·7928	+ 72	·7928	·8884	Loss ·0456	= 5·44
124.	Cd+Pt	18	·8500	+H_2SO_4 ·49	1·1646	+ 72	1·1888	·9184	Gain ·2254	= 24·6
125.	Cd+Pt	18	·8500	+H_2SO_4 ·49	·8214	+ 72	·8246	·8442	Loss ·0196	= 2·82

In each case dilution increased the *mean* direct electromotive force at the positive plate, and the *mean* counter electromotive force at the negative plate.

Table 81.—*Solutions of Neutral Salts.*

No. of Expt.	Voltaic Couple.	Grains of Water.	E. M. F. with Water.	Grains.	E.M.F with Solution.	Grains of Water.	E. M. F. after Dilution.	Calculated Mean E. M. F.	Change of Mean E. M. F. — Percent.
126.	Cd+Pt	18	·8500	+KCl ·745	·9878	+72	·9501	·8779	Gain ·1098 = 1·24
127.	Cd+Pt	18	·8500	+KCl ·745	·8299	+72	·8299	·8457	Loss ·0158 = 1·87
128.	Cd+Pt	18	·8500	+KBr ·119	·90148	+72	·9014	·8606	Gain ·0408 = 4·7
129.	Cd+Pt	18	·8500	+KBr ·119	·8214	+72	·8214	·8440	Loss ·0226 = 2·7
130.	Cd+Pt	18	·8500	+KI 1·66	·8814	+72	·8443	·8566	Loss ·0122 = 1·4
131.	Cd+Pt	18	·8500	+KI 1·66	·7785	+72	·7871	·8850	Loss ·0479 = 5·7
182.	Zn+Pt	18	1·127	+KI 1·66	1·1641	+72	1·1556	1·1348	Gain ·0208 = 1·74

Dilution increased the *mean* amount of direct electromotive force at the positive plates in Experiments 126, 128, and 182; and the *mean* counter electromotive force at the negative plate in Nos. 127, 129, and 181. The apparent exception in No. 180 was connected with the circumstance that the electromotive force with the diluted solution was less than that with water; this was avoided in No. 182 by using zinc as a positive metal.

Table 82.—*Solution of KCy.*

No. of Expt.	Voltaic Couple.	Grains of Water.	E. M. F. with Water.	Grains.	E.M.F with Solution.	Grains of Water.	E. M. F. after Dilution.	Calculated Mean E. M. F.	Change of Mean E. M. F. — Percent.
183.	Cd+Pt	18	·8500	+KCy ·65	·8448	+72	·8500	·8488	Gain ·0012 = ·14
184.	Cd+Pt	18	·8500	+KCy ·65	·7070	+72	·7213	·8209	Loss ·0996 = 12·14

Dilution increased the *mean* electromotive force at the positive plate in No. 183, and at the negative plate in No. 184.

Table 83.—*Solution of KHO.*

No. of Expt.	Voltaic Couple.	Grains of Water.	E. M. F. with Water.	Grains.	E.M.F with Solution.	Grains of Water.	E. M. F. after Dilution.	Calculated Mean E. M. F.	Change of Mean E. M. F. — Percent.
135.	Cd+Ag	18	·7642	+KHO ·56	·8500	+72	·8857	·7817	Gain ·054 = 6·91
136.	Cd+Ag	18	·7642	+KHO ·56	·7642	+72	·7642	·7642	Gain 0 = 0

The electromotive force in Experiment 186 was variable.

The results in these tables indicate that *dilution increased the mean amount of electromotive force in each case by removing farther asunder, and increasing the freedom of motion of the molecules of the active dissolved substance, and that this effect occurred at each plate, and was the same in kind at the negative as at the positive one, but less in degree at the former than at the latter.* They also show that when the freedom of motion of the molecules of the active dissolved substance is increased at the positive plate only, there is a " gain " of *mean* electromotive force of the couple, but if at the negative one only, there is usually a " loss ; " apparent slight exceptions occur in Nos. 121, 131, and 136.

Influence of Viscosity of the Electrolyte.

In order to examine the influence of viscosity upon the rate of increase of *mean* amount of electromotive force by dilution, a nine-tenths saturated solution of a salt having a high degree of viscosity was made by dissolving 60 grains of hydrated sulphate of beryllium in 5·0 cubic centimetres of water, the total volume and weight then being 7·0 cubic centimetres and 137·5 grains.

A series of diluted solutions were made by abstracting successive amounts of the strong solution and replacing them by water so as to produce equal increases of dilution. The total volume of solution used for each measurement of electromotive force was 7·0 c.c. The measurements were made with a zinc platinum couple in a similar manner to those of Tables 3 and 4, and the electromotive force of the most concentrated solution was the basis of calculation. The following are the results:—

TABLE 34.—*Solution of Sulphate of Beryllium.*

No. of Expt. 137.	Grains of BeSO₄	Actual E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	35·6	1·2986				
	32·6	1·2986	1·2843	Gain	·0143 =	1·1
	29·6	1·2986	1·2700	,,	·0286 =	2·24
	26·6	1·3014	1·2571	,,	·0443 =	3·51
	23·6	1·3014	1·2426	,,	·0588 =	4·74
	20·7	1·3014	1·2271	,,	·0743 =	6·05
	17·7	1·3014	1·2128	,,	·0886 =	7·32
	14·8	1·3014	1·1985	,,	·1029 =	8·58
	11·8	1·2957	1·1744	,,	·1218 =	10·33
	7·88	1·2900	1·1700	,,	·1200 =	10·25
	5·9	1·2843	1·1556	,,	·1287 =	11·14

By comparing these percentage numbers and the curve representing them with those of Tables 3 and 4 obtained with dilute solutions of chlorine and hydrochloric acid, it will be found that the rate of increase of gain of *mean* electromotive force by dilution was at a more rapid rate with the more viscous solution, as if the quicker diminution of viscosity increased the rate. In this case, as in the others, the increase of *mean* electromotive force varied directly as the dilution.

Some additional measurements were made with a zinc platinum couple, and a solution of potassium chloride before and after dissolving in it some ordinary gum arabic; the results are as follows:—

TABLE 35.

No. of Expt.	Grains.	Grains.	Grains.	E.M.F.
138.	74·5 KCl	+ 1800 H²O		1·2271 volt.
139.	74·5 KCl	+ 1800 H²O	+ 108 Gum	1·2271 volt.
140.	74·5 KCl	+ 1620 H²O	+ 108 Gum	1·2271 volt.

In these experiments viscosity had no apparent effect.

REMARKS ON SECTION B.

The numbers in Tables 16 to 23 show that the rates of change, *i.e.*, of increase or decrease of *mean* electromotive force, with different metals, by dilution of the same electrolyte, were

very different, and that the increase was often less or the decrease greater with electropositive metals giving large electromotive forces than with those giving smaller ones. In several cases, for instance, iron in KCy, thallium, sodium, or nickel, &c., in KHO, the simple electromotive force was smaller in the solution than in water alone, and occasioned "losses" of *mean* electromotive force.

Remarks on Sections A and B.

The results contained in these sections show that, notwithstanding the larger amount of water than of undiluted solution, and the smaller electromotive force excited by the former than by the latter, in no less than 22 out of 104 cases dilution failed to reduce the *simple* electromotive force of the solution, and in 17 out of those 22 the electromotive force was even greater after the dilution than previous to it. With solutions of halogens, acids, acid salts, and neutral ones, the simple electromotive force was nearly always decreased by dilution, but with alkaline ones (see Table 10) it was frequently increased unless a silver negative plate was substituted for the platinum one (see Table 11) and the action at the negative plate thus reduced. They also show that in nearly all cases, the changes of amount of *simple* electromotive force as found by experiment were different from those of *mean* electromotive force of the water and the undiluted solution; and that the *mean* electromotive forces were greater than those arrived at by calculation.

The results further show that an increase of freedom of motion of the molecules of the dissolved substance by means of dilution, without any such increase of freedom of those of either of the metals, is alone sufficient to increase the mean electromotive force at each of the metals, and consequently also the energy of chemical union of the electronegative dissolved substance with each of them. This is not unlike the circumstance that, in the case of mechanical impact of any two substances, the violence of collision and the amount of heat

evolved by it, are augmented by increasing the momentum of one only of the substances, and strongly supports the view that voltaic electromotive force and chemical union are consequences of molecular collision of the two chemically uniting substances. The increase of energy of the dissolved substance by dilution precedes that of mean electromotive force and of chemical union, and is a phenomenon entirely distinct from them; whether it increases the amount of heat of such union is a question I have not experimentally examined.

As dilution of the dissolved substance increases the *mean* amount of electromotive force at each metal, whilst it diminishes the number of molecules of that substance in contact with the metal; and as dilution cannot add to the mass or weight of a molecule, it probably produces an increase of molecular velocity, and this greater velocity more than counterbalances the loss of energy due to the smaller number and mass of colliding molecules. This largely agrees with the circumstance that "most salts, hydrated or anhydrous, dissolve in water with absorption of heat," and " those which absorb heat on solution, do also on dilution " (Watts's Dictionary of Chemistry, 3rd Suppt., p. 990).

The whole of the results in the two sections show that the amount of change of *mean* electromotive force of the voltaic couple by dilution varied largely with the kind of positive metal, of negative metal, and of electrolyte. And the experiments on "the influence of dilution at one metal only" prove that the direction and amount of *mean* electromotive force of the current is a result, not only of the action of the negative constituent of the liquid and the positive metal, but also of that of the same substance and the negative metal; that the latter action is the weakest; that the two actions are opposite and tend to neutralise each other, and that the final electromotive force is the difference of the two. It is, therefore, largely a deficiency of electropositive energy, which fits a conducting substance to act as the negative plate of a voltaic couple.

Neither a change of the kind of solvent nor a rise of temperature of the electrolyte prevented or appeared to diminish the gain of *mean* amount of electromotive force on dilution. (See Tables 14 and 15.) The influence of viscosity was only partly examined. The low positions of amalgams of potassium and sodium in Tables 16-20 and 21 were probably due to loss of molecular motion by some degree of chemical union between those metals and the mercury.

SECTION C.
Influence of Liquefaction of the Positive Metal with Different Metals and Electrolytes.

It is well known that amalgamation of zinc is attended by a slight increase of the electropositive condition of the zinc in dilute acids, notwithstanding that mercury is strongly negative to zinc in such liquids, and might, therefore, be expected to largely reduce the electromotive force. In the present section of this research I have examined this phenomenon and have ascertained the effects which amalgamation of different positive metals has upon their electromotive force.

In all the experiments of this section, and in the subsequent ones of dilution of the amalgams formed by addition of more mercury, the electrolyte was composed either of distilled water alone, or of one equivalent weight of the electrolytic substance in grains dissolved in 1,800 grains of water. In those of liquefaction, and in those of dilution, the kind of negative metal used in all cases except those of Tables 40 and 45 was platinum. The proportions of metal and mercury used in each liquefaction experiment were, an equivalent weight in grains of the positive metal, made up to 5,600 grains by addition of mercury to form a liquid amalgam; the actual amount of amalgam used, however, in each case was 100 grains. The amalgam was contained in a small glass cup at the end of a bent glass tube. (See Fig. 2).

Fig. 2.

The electromotive force of mercury with platinum in the given electrolyte was first measured, then that of the solid positive metal with platinum, and the mean amount of the two quantities calculated ; the amalgam was next formed, and its electromotive force with platinum in the electrolyte measured, and the difference between it and the calculated amount ascertained. (In Tables 40 and 45 silver was used in place of platinum.) In consequence of the smallness of the proportion of the positive metal dissolved in the mercury, and the quickness of solution of the superficial layer of its particles before the measurements could be made, the amounts of electromotive force, especially in the dilution experiments with alkali metal amalgams were lessened ; the measurements, therefore, were in all cases made as quickly as possible after preparing the amalgams, and the latter were not disturbed during the measurements, because it altered the electromotive force. The dry amalgam of magnesium quickly formed the black suboxide of that metal. Several kinds of electrolytes, acid, neutral, and alkaline, were employed. The following tables show the results :—

TABLE 86.—*Water.* Neg. metal Pt.

No. of Expt.	Positive Metal.	Grains.	E.M.F.		Grains of Hg.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		·0829							
141.	Mg	12·0	1·4700	+	5588	1·184	·0858	Gain 1·0982	=	1278·6
142.	Zn	32·5	1·1270	+	5667·5	1·163	·0904	,, 1·0709	=	1184·0
143.	Cd	56·0	·8500	+	5444·	·7407	·0905	,, ·6502	=	718·4
144.	Tl	204·0	·5720	+	5896·	·7092	·1010	,, ·2277	=	604·2
145.	Sn	59·	·6350	+	5541·	·6493	·0901	,, ·5606	=	601·4
146.	Pb	108·5	·6635	+	5496·5	·6063	·0936	,, ·5127	=	547·6
147.	Sb	40·5	·2481	+	5559·5	·8146	·0869	,, ·2277	=	262·0
148.	Bi	70·0	·2860	+	5530·	·8088	·0872	,, ·2216	=	254·0
149.	Cu	81·5	·2602	+	5568·5	·2431	·0858	,, ·1573	=	183·2
150.	Au	65·0	-·0858	+	5585·	·1201	·0809	,, ·0392	=	48·4

TABLE 87.—*Solution of ·865 grain HCL.*

No. of Expt.	Positive Metal.	Grains.	E.M.F.		Grains of Hg.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		·2288							
151.	Mg	12·0	1·7844	+	5588	1·6155	·2821	Gain 1·3380	=	576·4
152.	Zn	32·5	1·4643	+	5567·5	1·4759	·2389	,, 1·2420	=	580·9
153.	Cd	56·0	1·1217	+	5544·	·9928	·2854	,, ·7569	=	821·2
154.	Tl	204·0	·8866	+	5896·	·8580	·2525	,, ·6055	=	289·8
155.	Sn	59·0	·8066	+	5541·	·7551	·2847	,, ·5204	=	221·7
156.	Pb	108·5	·7878	+	5496·5	·7850	·2881	,, ·4967	=	208·7
157.	Bi	70·0	·5233	+	5580·	·6149	·2826	,, ·3823	=	164·8
158.	Cu	81·5	·4347	+	5568·5	·4847	·2296	,, ·2049	=	89·1
159.	Sb	40·5	·4719	+	5559·5	·4147	·2805	,, ·1842	=	79·9
160.	Au	65·0	·1287	+	5585·	·2481	·2276	,, ·0155	=	6·8

M. J. Regnault observed, and the above numbers confirm his observation, that whilst zinc, during its amalgamation by mercury becomes more electropositive in dilute acids, cadmium by amalgamation becomes less electropositive ; and he ascribes this difference to the fact that heat is absorbed during amalgamation in the former case and evolved in the latter one. (Comptes Rendus Acad. Sci., June 10, 1878. Chemical News, vol. xxxviii, p. 88.) But the above numbers further show that notwithstanding the adverse changes of thermal energy, the mean amount of electromotive force of cadmium in dilute hydrochloric acid was simultaneously increased 821·2 per cent., thus proving that the influence of the thermal change upon that force was small in comparison with that of increased freedom of molecular motion due to liquefaction.

Table 38.—*Solution of* ·745 *grain KCl.*

No. of Expt.	Positive Metal.	Grains.	E.M.F.		Grains of Hg.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		·1716							
161.	Mg	12·0	1·5701	+	5588·	1·5844	·1745	Gain 1·4099	=	807·9
162.	Zn	32·5	1·2271	+	5667·5	1·2885	·1777	,, 1·0608	=	596·9
163.	Cd	56·0	·9787	+	5444·	·8879	·1796	,, ·6583	=	366·5
164.	Sn	59·0	·7494	+	5541·	·7351	·1776	,, ·5575	=	313·9
165.	Pb	108·5	·6978	+	5496·5	·6921	·1803	,, ·5118	=	283·8
166.	Tl	204·0	·8008	+	5396·	·7264	·1945	,, ·5817	=	278·4
167.	Bi	70·0	·8718	+	5530·	·8489	·1741	,, ·1748	=	100·0
168.	Sb	40·5	·4290	+	5559·4	·8460	·1784	,, ·1726	=	99·5
169.	Cu	31·5	·3718	+	5568·5	·2631	·1727	,, ·0904	=	52·8
170.	Au	65·0	·1573	+	5535·	·1573	·1714	Loss ·0141	=	8·22

Table 39.—*Solution of* ·56 *grain KHO.*

No. of Expt.	Positive Metal.	Grains.	E.M.F.		Grains of Hg.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		-·0572							
171.	Zn	32·5	1·2185	+	5667·5	1·2414	-·0508	Gain 1·2922	=	2542·8
172.	Mg	12·0	1·4928	+	5588·	1·0410	-·0538	,, 1·0948	=	2034·94
173.	Sn	59·0	·9210	+	5541·	·8924	-·0468	,, ·9392	=	2006·8
174.	Pb	108·5	·8065	+	5496·5	·7686	-·0412	,, ·8048	=	1953·3
175.	Cd	56·0	·8843	+	5544·	·7121	-·0477	,, ·7598	=	1592·8
176.	Tl	204·0	·5434	+	5396·	·4433	-·0353	,, ·4786	=	1855·8
177.	Sb	40·6	·5005	+	5559·4	·5720	-·0581	,, ·6251	=	1177·3
178.	Bi	70·0	·8718	+	5530·	·2488	-·0518	,, ·8006	=	580·8
179.	Cu	31·5	·1716	+	5568·5	·1801	-·0558	,, ·2359	=	422·7
180.	Au	65·0	·0286	+	5535·	·0286	-·0561	,, ·0847	=	150·9

In the next table of measurements a silver negative plate was employed.

TABLE 40. *Solution of ·56 grain KHO. Negative metal Ag.*

No. of Expt.	Positive Metal.	Grains.	E.M.F.		Grains of Hg.	E.M.P.	Calculated E.M.F.	Change of Mean E.M.F.	Per cent.
	Hg		·00						
181.	Zn	82·5	1·2700	+	5667·5	1·2986	·0073	Gain 1·2913 =	17689·
182.	Sb	40·6	·9782	+	5550·4	·6549	·00477	,, ·6501 =	18629·
183.	Cu	81·5	·2860	+	5568·5	·2860	·00228	,, ·2837 =	12448·
184.	Sn	59·	·9782	+	5541·	1·0068	·0103	,, ·9965 =	9674·
185.	Cd	56·	·9156	+	5544·	·7928	·0092	,, ·7886 =	8517·
186.	Au	65	·07436	+	5585·	·0629	·0009	,, ·0620 =	6888·
187.	Bi	70	·4318	+	5580·	·3718	·00539	,, ·3664 =	6798·
188.	Pb	103·5	·7498	+	5496·5·	·7493	·0138	,, ·7355 =	5829·
189.	Tl	204·0	·6635	+	5396·0	·5720	·0241	,, ·5479 =	2273·

The percentage gains of *mean* amount of electromotive force were greatly increased by the use of a silver negative plate.

REMARKS ON SECTION C.

Notwithstanding the very large proportion of mercury to that of the dissolved metal, and the usually very much greater electronegative character of the mercury, in no less than forty-eight cases out of forty-nine, liquefaction of the positive metal was attended by an increase of *mean* amount of electromotive force ; and in twelve out of the forty-eight cases (four of these being with zinc) the *simple* electromotive force was even greater after the liquefaction than previous to it. The exceptional case was gold in solution of KCl. (See Experiment 170.)

The whole of the instances of this section show that *liquefaction of the positive metal of a voltaic couple by means of mercury, increased its electromotive force, and indicate that this increase was due to greater freedom of motion of the molecules of the liquefied metal.*

The results also indicate that an increase of freedom of motion of the molecules of the positive metal by means of solution in mercury, without any such increase of freedom of those of the electrolyte, is alone sufficient to increase the *mean* electromotive force and energy of chemical union of that metal with the electronegative ingredient of the electrolyte. This appears similar to the effects of mechanical collision of two solids, and supports the view that volta-electromotive force and its attendant energy of chemical union are due to mechanical impact of the two uniting substances. (See p. 97.)

The whole of the results of this section further show that the amount of change of *mean* electromotive force varied with the kind of positive metal, of negative metal, and of the electrolyte. How far the decreases of *simple* electromotive force of the amalgam of magnesium in Tables 86, 87, and 89 were due to chemical union of the two metals, I have not examined ; it did not occur in a solution of KCl.

D.—*Influence of Dilution of the Positive Amalgam, with different Metals and Electrolytes.*

It is already known that by diluting an amalgam of zinc by addition of more mercury, the electromotive force of the

amalgam when immersed in certain electrolytes is not much decreased. Hockin and Taylor (Jour. Teleg. Engrs., 1879), and Lindeck (Ann. Phys. und Chem., 1889) [2] 35, pp. 311, 331. The Electrician, July 5, 1889, p. 214), observed that the proportion of zinc contained in a solution of that metal in mercury may vary from a mere trace to a very large amount without altering the electromotive force of the current excited by it in a solution of sulphate of zinc. From this circumstance, together with the fact that mercury is electronegative to zinc in that liquid, it necessarily follows that the *mean* amount of electromotive force of the amalgam must be *increased* by the addition of the less electropositive substance. The calculated *mean* electromotive force of a mixture of 5,600 parts of zinc amalgam having an electromotive force of 1·1613 with platinum in water, and 50,400 parts of mercury having an electromotive force of ·0829, must necessarily be very much less than 1·1270 which is the number it actually gave. (See Expt. 192.) Further, in such a case, if the simple electromotive force of the amalgam is diminished by the act of dilution, but at a lesser rate than that of the zinc in it is increased by the greater degree of freedom of its molecules, the *mean* amount of such force of the amalgam must still be increased by the dilution.

In making and using the amalgam in the following experiments, one equivalent weight in parts of the positive metal was dissolved in sufficient mercury to form 5,600 parts by weight, and after measuring the electromotive force excited by the amalgam, the proportion of mercury was increased about ten times, or such as to form a total weight of 56,000 parts of amalgam, and the force again measured ; the actual quantity of mercury used, however, was sufficient to make 100 grains of the concentrated amalgam, and 10 grains of this was mixed with 90 grains of pure mercury to form the dilute amalgam.

The negative metal employed in each case, unless otherwise specified, was platinum, and the electromotive force of it with mercury in water was = ·0829 volt. The union of magnesium with mercury was attended by slight explosive action.

TABLE 41.—*Water.* Neg. metal Pt.

No. of Expt.	Positive Amalgam.	Grains of Amalgam.	E.M.F. ·0829		Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
190.	Na + Hg	5600	2·2006	+	50400	1·800	·2496	Gain 1·5054 =	511·0
191.	K + Hg	5600	2·3092	+	50400	1·8574	·3055	,, 1·5519 =	507·9
192.	Zn + Hg	5600	1·1613	+	50400	1·1270	·1873	,, ·9897 =	501·7
193.	Cd + Hg	5600	·7407	+	50400	·7407	·1486	,, ·5921 =	398·4
194.	Tl + Hg	5600	·7092	+	50400	·7092	·1455	,, ·5687 =	387·4
195.	Sn + Hg	5600	·6443	+	50400	·6850	·1395	,, ·4955 =	355·2
196.	Pb + Hg	5600	·6068	+	50400	·5977	·1852	,, ·4625 =	342·5
197.	Mg + Hg	5600	1·1840	+	50400	·8408	·1980	,, ·6478 =	385·6
198.	Bi + Hg	5600	·8088	+	50400	·8088	·1054	,, ·2084 =	192·9
199.	Sb + Hg	5600	·8146	+	50400	·8008	·1060	,, ·1948 =	183·8
200.	Cu + Hg	5600	·2481	+	50400	·2288	·0989	,, ·1299 =	131·3
201.	Au + Hg	5600	·1201	+	50400	·0858	·0866	Loss ·0008 =	·92

The results of Nos. 191 and 197 were very variable.

TABLE 42.—*Solution of ·865 Grain HCl.*

No. of Expt.	Positive Amalgam.	Grains of Amalgam.	E.M.F.		Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		·2288							
202.	K + Hg	5600	2·5950	+	50400	2·2292	·4654	Gain 1·7638	=	378·9
203.	Na + Hg	5600	2·4580	+	50400	2·0402	·4517	,, 1·5885	=	351·6
204.	Zn + Hg	5600	1·4759	+	50400	1·4416	·3595	,, 1·090	=	308·3
205.	Tl + Hg	5600	·8580	+	50400	·8580	·2917	,, ·5670	=	194·3
206.	Cd + Hg	5600	·9923	+	50400	·8980	·3051	,, ·5929	=	194·3
207.	Mg + Hg	5600	1·6158	+	50400	1·0410	·3675	,, ·6735	=	183·3
208.	Pb + Hg	5600	·7850	+	50400	·7850	·2794	,, ·4556	=	163·0
209.	Sn + Hg	5600	·7551	+	50400	·7286	·2814	,, ·4422	=	157·1
210.	Bi + Hg	5600	·6149	+	50400	·5148	·2674	,, ·2474	=	92·5
211.	Cu + Hg	5600	·4847	+	50400	·4004	·2498	,, ·1151	=	46·17
212.	Sb + Hg	5600	·4147	+	50400	·8460	·2478	,, ·0987	=	39·91
213.	Au + Hg	5600	·2431	+	50400	·2431	·2802	,, ·0129	=	5·6

The results of Nos. 202, 203, and 204 were variable.

TABLE 48.—*Solution of ·745 grain KCl.*

No. of Expt.	Positive Amalgam.	Grains of Amalgam.	E.M.F.		Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		·1716							
214.	Mg + Hg	5600	1·5844	+	50400	1·5272	·3128	Gain 1·2144	=	388·2
215.	Zn + Hg	5600	1·2385	+	50400	1·2385	·2782	,, ·9608	=	345·1
216.	Cd + Hg	5600	·8879	+	50400	·8150	·2881	,, ·5769	=	242·3
217.	Sn + Hg	5600	·7851	+	50400	·7832	·2279	,, ·5043	=	221·2
218.	Tl + Hg	5600	·7293	+	50400	·7264	·2273	,, ·4991	=	219·5
219.	Pb + Hg	5600	·6971	+	50400	·6892	·2286	,, ·4656	=	208·2
220.	Bi + Hg	5600	·3489	+	50400	·8432	·1893	,, ·1539	=	81·8
221.	Sb + Hg	5600	·3460	+	50400	·3174	·1891	,, ·1284	=	67·9
222.	Cu + Hg	5600	·2681	+	50400	·2574	·1807	,, ·0767	=	42·4
223.	Au + Hg	5600	·1578	+	50400	·1115	·1701	Loss ·0586	=	34·4

The results of No. 214 were very variable and inaccurate.

TABLE 44.—*Solution of* ·56 *grain KHO.*

No. of Expt.	Positive Amalgam. Hg	Grains of Amalgam.	E.M.F.		Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of mean E.M.F.	Per cent.
224.	Tl + Hg	5600	·4719	+	50400	·4488	-·0043	Gain ·4476 =	-10409·8
225.	Sb + Hg	5600	·5720	+	50400	·5863	·0057	,, ·5806 =	10186·0
226.	Cd + Hg	5600	·7121	+	50400	·7149	·0197	,, ·6952 =	3528·9
227.	Pb + Hg	5600	·7636	+	50400	·7498	·0248	,, ·7245 =	2921·3
228.	Sn + Hg	5600	·8924	+	50400	·8638	·0877	,, ·8261 =	2190·9
229.	Zn + Hg	5600	1·2414	+	50400	1·2414	·0726	,, 1·1688 =	1690·9
230.	Bi + Hg	5600	·2488	+	50400	·2860	-·0266	,, ·3126 =	-1175·1
231.	Mg + Hg	5600	1·0410	+	50400	·6263	·0526	,, ·5787 =	1090·6
232.	Cu + Hg	5600	·1801	+	50400	·2802	-·0384	,, ·8186 =	-987·1
233.	Au + Hg	5600	·0348	+	50400	·0286	-·0480	,, ·0766 =	-159·45

As the negative numbers in the preceding table were probably due to the action of the potash upon the platinum plate, in the next two series of experiments silver was used instead of platinum to form with cadmium the voltaic couple.

TABLE 45.—*Solution of* ·56 *grain KHO.* Negative metal Ag.

No. of Expt.	Positive Amalgam. Hg	Grains of Amalgam.	E.M.F. ·00		Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of mean E.M.F.	Per cent.
284.	Cu + Hg	5600	·2860	+	50400	·3482	·0286	Gain ·3146 =	1100·0
285.	Sb + Hg	5600	·6263	+	50400	·6435	·0626	,, ·5809 =	927·9
236.	Pb + Hg	5600	·7498	+	50400	·7498	·0749	,, ·6744 =	918·7
237.	Bi + Hg	5600	·8718	+	50400	·4919	·0371	,, ·8347 =	902·1
288.	Cd + Hg	5600	·9072	+	50400	·9072	·0907	,, ·8165 =	900·2
239.	Au + Hg	5600	·0629	+	50400	·05148	·00629	,, ·0566 =	900·0
240.	Zn + Hg	5600	1·2986	+	50400	1·2986	·1298	,, 1·1682 =	900·0
241.	Tl + Hg	5600	·5720	+	50400	·5233	·0572	,, ·4661 =	814·8
242.	Sn + Hg	5600	1·0068	+	50400	·8924	·1006	,, ·7918 =	787·0

*Rate of Variation of Mean Electromotive Force by Dilution of
the Positive Amalgam.*

In order to ascertain whether the effects of successive
additions of equal quantities of mercury upon the percentage
gain of mean amount of electromotive force were equal, or
whether that of each succeeding addition was less, I made a
series of measurements with a negative plate of platinum and a
positive amalgam of cadmium. The following are the results :—

TABLE 46.—*Solution of ·865 grain of HCl in 18 grains of Water.*

No. of Expt. 243.	Grains of Cd. Amalgam.	Grains of	E.M.F.	Calcul'd Mean E. M. F.	Change of Mean E. M. F.		Per cent.
	56 in	5,600	·9980				
	56 ,,	10,640	·9901	·6310	Gain ·3591	=	56·9
	56 ,,	15,680	·9844	·5017	,, ·4827	=	96·2
	56 ,,	20,720	·9787	·4353	,, ·5434	=	124·8
	56 ,,	25,760	·9701	·3949	,, ·5752	=	145·6
	56 ,,	30.800	·9615	·3677	,, ·5938	=	161·4
	56 ,,	35,840	·9529	·3482	,, ·6047	=	173·3
	56 ,,	40,880	·9415	·3334	,, ·6081	=	182·4
	56 ,,	45,920	·9300	·3220	,, ·6080	=	188·8
	56 ,,	50,960	·9157	·3127	,, ·6030	=	193·2
	56 ,,	56,000	·8986	·3051	,, ·5935	=	194·5

According to these results, the gain of percentage *mean*
amount of electromotive force varied directly as the degree of
dilution, the same as occurred by diluting electrolytes with
water (see Tables 3 and 4) ; but in the present case, whilst the
dilution was uniform throughout, the electromotive force
increased at a diminishing rate, slowly at first, the greatest gain
being with the first dilution, but rapidly at last, and approached
a limit at the last dilution ; this may be more clearly perceived
by graphically delineating it by means of a curve representing
the differences of percentage amount.

As this diminishing rate of increase was probably due to a
comparatively slow supply of cadmium by diffusion from the
interior of the amalgam to its surface in proportion to the
speed of solution by the acid, another series of experiments were
made with a less corrosive solution of potassium chloride and
zinc amalgam, the negative metal being again platinum. The
following table contains the results :—

TABLE 47.—*Solution of* ·745 *grain KCl in* 18 *grains* H^2O.

No. of Expt. 244.	Grains of Zinc.	Grains of Amalgam.	E.M.F.	Calcul'd Mean E. M. F.	Change of Mean E. M. F.	Per cent.
	32·5	in 5,600	1·2385			
	32·5	,, 10,640	1·2385	·7331	Gain ·5054 =	68·9
	32·5	,, 15,680	1·2385	·5526	,, ·6859 =	124·0
	32·5	,, 20,720	1·2385	·4600	,, ·7785 =	169·2
	32·5	,, 25,760	1·2385	·4085	,, ·8350 =	206·9
	32·5	,, 30,800	1·2385	·3655	,, ·8730 =	238·8
	32·5	,, 35,840	1·2385	·3382	,, ·9003 =	266·3
	32·5	,, 40,880	1·2385	·3177	,, ·9208 =	289·8
	32·5	,, 45,920	1·2385	·3016	,, ·9369 =	310·2
	32·5	,, 50,960	1·2385	·2888	,, ·9497 =	328·6
	32·5	,, 56,000	1·2385	·2782	,, ·9602 =	345·1

The curve which represents the differences of percentage amount of *mean* electromotive force in this case more nearly approaches a straight line ; as if the supply of positive metal was more equal to the rapidity of its solution than in Table 46.

As in the case of different positive metals amalgamated with mercury some would dissolve in the same electrolyte much more rapidly than others, and this would affect the magnitude of the percentage gain of *mean* electromotive force, some experiments were made to obtain an approximate idea of the rates at which several different electropositive metals diffused through mercury and renewed the action at its surface.

A glass tube of the annexed form (see Fig. 8), and open at both ends, was filled with pure mercury from A to B, and with the electrolyte from B to C. A much smaller one, D, with a cup-shaped extremity, and containing mercury, was suspended in the electrolyte, and the two portions of mercury connected by means of platinum wires with a suitable galvanometer. A freshly formed fragment of amalgam of the metal of known composition, was gently placed upon the mercury at A, and the time which elapsed before the galvanometer needles moved was noted. Before adding the amalgam it was ascertained that the needles were at zero, and that a slight disturbance of the mercury did not affect them. The length of the column of mercury from surface to surface was about 1·5 inches. The weight of amalgam added was 5·0

grains ; and each amalgam contained ·78 grain of metal dissolved in 25 grains of mercury.

Fig. 3.

The following are the results :—Zinc diffused in 2 hours 15 minutes; tin, 2 hours 30 minutes; lead, 2 hours 40 minutes; cadmium, 3 hours; sodium, 3 hours 50 minutes; and potassium, 5 hours 45 minutes. The rapidity of diffusion was evidently largely affected by the specific gravity of the metal. It is manifest from these results that the rates of diffusion of unlike metals in mercury are very different ; and this may affect the influence of the rate of dilution of metals by mercury upon the rate of variation of the mean amount of electromotive force of their amalgams.

REMARKS ON SECTION D.

The chief conclusions to be drawn from the results of the experiments of this section are similar to those of Section C,

and need not be repeated; and nearly all the remarks made on that section are applicable to this one.

The effects of *dilution* of the positive amalgam upon the *mean* amount of electromotive force were substantially the same as those of *liquefaction* of the solid positive metal, but were less in amount. Thus, on comparing the percentage amount of gain of *mean* electromotive force obtained on liquefying 56 grains of cadmium by means of 5,544 grains of mercury in Experiment No. 153, Table 37, with that obtained by diluting the resulting amalgam with 5,040 grains of mercury in the first dilution of Table 46, it is found that the effect of the former was 5·6 times greater than that of the latter, and this agrees with the successively diminishing effects of equal further additions of mercury in Table 46. (See also Tables 56 and 57.)

Notwithstanding that in 52 out of the 53 cases of dilution in Section D, mercury was less electropositive towards platinum than the amalgam to which it was added, in no less than 7 cases the simple electromotive force was increased, and in 11 it was not diminished, whilst in the remaining 35 it was diminished less than the calculated amount, and the *mean* electromotive force was increased in 51 out of the total 53 instances. All the seven increases of simple electromotive force were with copper, antimony, bismuth, and cadmium in solution of caustic potash. There were two cases of loss of *mean* electromotive force in 53 experiments of dilution with mercury, but only one in 49 experiments of liquefaction by mercury. The only two cases of decrease of *mean* electromotive force, Nos. 201 and 223, were with gold amalgam in water and in solution of potassium chloride. All the variable results occurred with the most highly electropositive amalgams, especially that of magnesium.

As in Tables 36, 37, and 39, decreases of *simple* electromotive force occurred by *liquefaction* of magnesium, but not in a solution of KCl, by means of mercury, so also in Tables 41, 42, and 44, similar decreases occurred with that metal by *dilution* of its amalgam, excepting in the electrolyte mentioned.

The effects of diluting the positive amalgam are usually more simple than those of diluting the electrolyte, because the latter affects the electromotive forces at *both* electrodes.

Section E.

Influence of Liquefaction and Dilution of the *Negative* Metal.

The following experiments were made in this section. In each experiment an equivalent weight in grains of the negative metal was dissolved in a sufficient quantity of mercury to form 5,600 grains of amalgam. The positive metal in each case was zinc.

1.—Liquefaction of the Negative Metal.

Table 48.—*Water.*

No. of Expt.	Negative Metal	Grains	E.M.F.	Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
245.	Hg Cu	31·5	1·0481 1·0984	+ 5568·5	1·0412	1·0482	Loss ·007	=	·66

Table 49.—*Solution of ·865 grain HCl.*

246.	Hg Cu	31·5	1·2700 1·1556	+ 5568·5	1·1127	1·2692	Loss ·1565	=	12·80

Table 50.—*Solution of ·745 grain KCl*

247.	Hg Cu	31·5	1·1584 1·0818	+ 5568·5	1·0840	1·1574	Loss ·0788	=	6·33

Table 51.—*Solution of ·56 grain KHO.*

248.	Hg Cu	31·5	1·1784 1·0955	+ 5568·5	1·1120	1·1778	Loss ·0658	=	5·59

The results of each of these four experiments indicate that liquefaction increased the *mean* counter electromotive force and chemical energy of the negative plate, thereby decreasing the direct electromotive force of the current.

In the following *dilution* experiments the proportion of mercury in the amalgam was increased to nearly ten times its original amount.

2.—Dilution of the Negative Amalgam.

TABLE 52.—*Water.*

No. of Expt.	Negative Metal.	Grains.	E.M.F.	Grains of Hg.	E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.		Per cent.
	Hg		1·0481						
249.	Au +	Hg 5600	1·1012	+ 50400	1·1012	1·0584	Gain ·0478	=	4·58
250.	Cu +	Hg 5600	1·0412	+ 50400	1·0469	1·0474	Loss ·0005	=	·047

TABLE 53.—*Solution of* ·865 *grain HCl.*

	Hg		1·2700						
251.	Au +	Hg 5600	1·2737	+ 50400	1·2757	1·2705	Gain ·0052	=	·40
252.	Cu +	Hg 5600	1·1127	+ 50400	1·1270	1·2542	Loss ·1270	=	10·16

TABLE 54.—*Solution of* ·745 *grain KCl.*

| | Hg | | 1·1584 | | | | | | |
| 253. | Cu + | Hg 5600 | 1·0841 | + 50400 | 1·0984 | 1·5160 | Loss ·0526 | = | 4·57 |

TABLE 55.—*Solution of* ·56 *grain KHO.*

| | Hg | | 1·1784 | | | | | | |
| 254. | Cu + | Hg 5600 | 1·1127 | + 50400 | 1·1270 | 1·1718 | Loss ·044 | = | 3·76 |

The amalgam in Experiment 254 quickly became covered with a film. N.B.—The *losses* of *mean* electromotive force of the current are equal to *gains* of electromotive force at the negative plate.

In each of these ten cases the effect was comparatively small, nearly all the effects were losses, and the largest gain was 4·53 per cent. ; the exceptional instances were with gold amalgam, the same as in Experiments 170, 201, and 223 of liquefaction and dilution of the *positive* metal. If we compare these results obtained with copper as a negative metal with those yielded by it as a positive one in the same liquids in Experiments 149, 158, 169, 179, and 183, and in 200, 211, 222, 232, and 234, we find that whilst they were all large gains with it as a positive metal they were all small losses with it as a negative one. (See Tables 56 and 57.) All these results agree with the fact that the negative metal is not an active cause but only a necessary condition (and in the case of polarisation a hindrance) of the voltaic current.

TABLE 56.—*Cu as Positive Metal.*

	By Liquefaction.				By Dilution.		
In Water	Expt. 142.	Gain	183·2	Expt.	193.	Gain	131·3
In HCl	,, 151.	Gain	89·1	,,	204.	Gain	46·17
In KCl	,, 162.	Gain	52·3	,,	215.	Gain	42·4
In KHO	,, 172.	Gain	− 422·7	,,	225.	Gain	− 987·1
In KHO	,, 176.	Gain	12443·0	,,	227.	Gain	1100·0

TABLE 57.—*Cu as Negative Metal.*

	By Liquefaction.				By Dilution.		
In Water	Expt. 237.	Loss	·66	Expt.	250.	Loss	·047
In HCl	,, 238.	Loss	12·20	,,	252.	Loss	10·16
In KCl	,, 239.	Loss	6·33	,,	253.	Loss	4·57
In KHO	,, 240.	Loss	5·59	,,	254.	Loss	3·76

In both these groups of cases the effect of the dilution was to increase the degree of freedom of molecular motion of the copper, and therefore to make it more positive as a positive metal and less negative as a negative one. The effect of liquefaction was in all these cases greater than that of dilution.

Both by the influence of liquefaction and by that of

dilution of the negative metal, the *mean* amount of direct electromotive force was most diminished in dilute hydrochloric acid and least in water, and greatest in that liquid which had most chemical action upon the copper.

Remarks on Section E.

All the results of this section confirm the conclusion that both liquefaction and dilution of the negative metal, by enlarging the freedom of motion of its molecules, augments the chemical action of the liquid upon it, and simultaneously increases its electropositive and decreases its electronegative state, produces counter electromotive force, and consequently *lessens* the mean amount of direct electromotive force and current.

Section F.
Influence of Diluting one Solid Metal by means of another.

In order to ascertain whether the dilution of a solid metal by another affected the *mean* amount of electromotive force, I made a series of alloys and measured their electromotive forces, and that of their constituent metals, with a negative plate of platinum in dilute hydrochloric acid containing one equivalent of HCl in grains in 1,800 grains of water. Care was taken to employ pure metals, to mix the alloys thoroughly without much oxidation, and to prevent liquation of the metals. The alloy which constitutes the middle term* of the series in Tables 58 and 59 was composed of equivalent proportions of the two constituents. The following are the results of the measurements :—

Table 58.—*Zinc + Bismuth in dilute HCl.*

No. of Expt.	Parts of Zn.	Parts of Bi.	E.M.F.	Calculated E.M.F.	Change of Mean E.M.F.	Per cent.
	32·5		1·4702			
255.	32·5	14	1·3844	1·1851	Gain ·1993 =	16·8
256.	32·5	28	1·3415	1·0319	,, ·3096 =	30·0
257.	32·5	42	1·2728	·9364	,, ·3364 =	35·9
258.	32·5	56	1·2271	·8710	,, ·3561 =	40·9
259.	32·5	70· *	1·1699	·8235	,, ·3464 =	42·9
260.	26·	70·	1·1613	·7797	,, ·3816 =	48·9
261.	19·5	70·	1·1556	·7296	,, ·4260 =	58·4
262.	13·0	70·	1·1498	·6716	,, ·4782 =	71·2
263.	6·5	70·	1·1413	·6087	,, ·5376 =	89·0
		70·	·5233			

* Bi²Zn³.

As the whole of the changes of *mean* electromotive force were *gains*, there was probably no chemical union between the two metals ; all the alloys behaved like zinc simply diluted, and thus showed that dilution or simple increase of volume increased the mean electromotive force of metals even in the solid state. The chief difference between dilution of zinc by means of bismuth and by means of mercury appears to be that the latter produces greater effects owing to its liquefying the metal and thus imparting greater freedom of molecular motion. (See Experiment 157.) The increases of gain in the above table were irregular in amount.

TABLE 59.—*Zinc + Tin in dilute HCl.*

No. of Expt.	Parts of Zn. 65	Parts of Sn.	E. M. F.	Calculated E.M.F.	Change of Mean E.M.F.		Per cent.
	65		1·4702				
264.	65	23·6	1·2900	1·2940	Loss ·004	=	·3
265.	65	47·2	1·2356	1·1919	Gain ·0437	=	3·67
266.	65	70·8	1·1842	1·1254	,, ·0588	=	5·21
267.	65	94·4	1·1556	1·0786	,, ·0770	=	7·13
268.	65	118·0*	1·1270	1·0439	,, ·0831	=	7·96
269.	52	118·0	1·0841	·9064	,, ·1780	=	19·63
270.	39	118·0	1·0269	·8882	,, ·1387	=	15·61
271.	26	118·0	·9268	·8665	,, ·0603	=	6·96
272.	13	118·0	·8410	·8409	,, ·0001	=	·01
		118·0	·8094				

* ZnSn.

Nearly all the effects in this series were gains of mean electromotive force, and showed that dilution increased the electromotive force of the substance diluted, even when the substance remained in the solid state. The changes showed very little evidence of chemical union between the two metals, and if there was any it was very feeble, and was almost entirely disguised by the greater influence of dilution. The effects were less simple than those produced by solution and dilution of either metal by means of mercury, probably in consequence of the usually greater molecular complexity of metals in the solid than in the liquid state. The alloys behaved neither like zinc

alone nor like tin alone ; the addition of zinc diluted the tin, and that of tin diluted the zinc. Zinc having nearly double the electromotive force of tin, its addition as a diluent to tin increased the *mean* electromotive force more rapidly than the addition of tin to zinc, and the maximum gain of mean electromotive force was therefore not with equivalent proportions of the two metals, but with 1·0 equivalent of zinc added to 1·2 equivalent of tin. The *simple* electromotive force of the mixtures varied throughout the series directly as the proportion of zinc and inversely as that of tin, and did not as completely show the phenomena which occurred as the changes of *mean* electromotive force.

It is necessary in cases of *dilution* of alloys to select, if possible, a pair of metals in which the effect is not disguised by that of chemical union, and in which each metal of the pair dissolves freely in the other.

TABLE 60.—*Tin + Copper in dilute HCl.*

No. of Expt.	Parts of Sn.	Parts of Cu.	E.M.F.	Calculated E. M. F.	Change of Mean E. M. F.	Per cent.
	118·		·8066			
273.	59·	63·4	·7208	·6145	Gain ·1063 =	17·81
274.	39·8	63·4	·5063	·5776	Loss ·0713 =	12·3
275.	32·2	63·4	·4348	·5600	,, ·1252 =	22·3
276.	29·5	63·4	·4348	·5526	,, ·1178 =	21·8
277.	23·6	63·4	·4348	·5310	,, ·0962 =	18·1
		63·4	·4347			

Experiment $273 = Cu^3Sn$; $274 = Cu^3Sn$; $275 = Cu^{18}Sn^5$; $276 = Cu^4Sn$; and $277 = Cu^5Sn$.

Both the simple and the calculated electromotive forces varied directly as the proportion of the more positive metal tin ; but the fact of large losses of mean electromotive force occurring, indicated a considerable degree of chemical union between the two metals.

TABLE 61.—*Aluminium Bronze in dilute HCl.*

This alloy contained " 5 per cent. of aluminium," and gave the following effects :—

No. of Expt.		E.M.F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
	Al.	1·1297			
278.	Al bronze.	·4875	·4694	Loss ·0319 = 6·78	
	Cu.	·4347			

The *loss* of *mean* electromotive force indicates that the alloy is a chemical compound.

Determinations of the amount of *simple* electromotive force only, yielded by various alloys of copper and zinc when used as the positive plate of a voltaic cell, have been made by A. P. Laurie (Jour. Chem. Soc., 1888, vol. liii., p. 104), and are given in the three first columns of Table 62; and I have calculated from the given numbers, the *mean* electromotive forces and percentage changes of such force of the zinc and copper in the alloys as follows :—

TABLE 62.—*Copper + Zinc as a Positive Plate.*

Parts of Zinc.	Parts of Copper.	E.M.F. in Volts	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
	100·	− ·020			
25·	75·	− ·020	·1350	Loss ·1370 =	101·4
44·6	55·4	+ ·040	·2566	Loss ·2160 =	84·3
49·5	50·5	·070	·2860	Loss ·2160 =	75·5
50·7	49·3	·070	·2946	Loss ·2246 =	76·1
52·8	47·2	·075	·3070	Loss ·232 =	75·5
53·9	46·1	·065	·3142	Loss ·249 =	79·3
56·1	43·9	·070	·3279	Loss ·257 =	78·3
58·3	41·7	·080	·3407	Loss ·260 =	76·4
63·0	37·0	·085	·3700	Loss ·285 =	77·0
63·5	36·5	·085	·3737	Loss ·288 =	77·0
64·1	35·9	·160	·3775	Loss ·216 =	57·5
66·2*	33·8	·530	·3905	Gain ·140 =	35·9
66·8	33·2	·520	·3942	Gain ·126 =	32·0
68·1	31·9	·540	·4022	Gain ·138 =	34·3
69·7	30·3	·570	·4122	Gain ·158 =	38·3
77·0	23·0	·600	·4574	Gain ·143 =	31·3
83·6	16·4	·580	·4983	Gain ·081 =	16·2
87·6	12·4	·590	·5231	Gain ·067 =	12·8
96·5	3·5	·590	·5788	Gain ·081 =	5·3
100·		·600			

$* = Zn^3Cu.$

According to these numbers—First, the formation of any alloy of zinc and copper was attended by a change, either a loss or gain, of mean electromotive force of the two metals. Second, in forming any such alloy containing *more* than 34· per cent. of copper, the act of· mixing the two metals was attended by a *loss* of mean amount of electromotive force, and the alloy therefore contained a chemical compound; the first added quantity of zinc produced the largest percentage of loss, and therefore united with the greatest degree of chemical energy with the copper. Third, in forming any such alloy containing *less* than 34· per cent. of copper, the mixture of the metals was attended by a *gain* of mean electromotive force, showing that one metal diluted the other ; and as the mean of that force increased with the increase of copper, that metal diluted the more positive one zinc. Fourth, by increasing the proportion of copper above 34· per cent., a sudden change occurred attended by a large loss of electromotive force and a considerable degree of chemical union ; and by further increase of copper to 75· per cent, the percentage of loss of mean electromotive force augmented largely but irregularly ; and, Fifth, dilution of zinc by copper operated probably not only in all the alloys containing less than 34· per cent. of copper, but probably in some of those which contained more, and in which its action was disguised by the greater influence of chemical union.

In such cases as this, as in all others in this research, it is necessary to ascertain not only the changes of *simple* electromotive force of the *mixtures*, but also those of *mean* electromotive force; first, because each of the substances takes part in the action ; and second, because the phenomena can then be more completely explained than if the *simple* electromotive force only is determined. For additional cases of probable chemical union of potassium, sodium, and magnesium with mercury, see Tables 16, 20, 21, 36, 37, 38, 39, 41, 42, 43 and 44. In some cases a chemical alloy is first formed and then dissolves in the excess of the diluting metal.

I did not consider it necessary to make a series of experiments with alloys as *negative* metals.

RELATION OF VOLTA-ELECTROMOTIVE FORCE TO EQUIVALENT VOLUMES OF ELEMENTARY SUBSTANCES.

The general truth, that increase of volta-electromotive force and chemical energy of substances by dilution is due to increase of equivalent volume, is not limited to cases of liquefaction of metals, dilution of amalgams and electrolytes, and of solid metals by each other, but is of a much more fundamental and extensive character. The following examples show that in a very large proportion of cases, though not manifestly in all, those elementary substances, both metals and metalloids, which exhibit the greatest electromotive force and chemicoelectric energy, are those which contain the smallest number of equivalent weights per volume ; and the less energetic ones are those of small equivalent volume (other investigators have observed this circumstance). The following list includes nearly all the most common of those substances. The equivalent volumes were obtained by dividing the equivalent weights by the specific gravities.

Table 63.—*Equivalent Volumes of Elementary Substances.*

Metal.	Valency	Atomic Weight.	Equival'nt Weight.	Specific Gravity.		Equival'nt Volume.
Caesium ...	I.	132·9	132·9	Solid	1·88	70·69
Rubidium	I.	85·5	85·5	,,	1·52	56·25
Potassium	I.	39·1	39·1	,,	·87	44·95
Sodium ...	I.	23·05	23·05	,,	·978	23·56
Lithium ...	I.	7·02	7·02	,,	·59	11·9
Thallium ...	I.	204·18	204·18	,,	11·85	17·22
Silver	I.	107·92	107·92	,.	10·53	10·25
Barium ...	II.	137·0	68·5	,,	3·75	18·266
Strontium	II.	87·6	43·8	.,	2·54	17·244
Calcium ...	II.	40·0	20·0	,,	1·57	12·74
Lead	II.	206·95	103·47	,,	11·37	9·10
Tin	II.	119·0	59·5	,,	7·29	8·16
Magnesium	II.	24·8	12·15	,,	1·74	6·98
Zinc.........	II.	65·3	32·65	,,	7·15	4·56
Cadmium	II.	112·0	56·0	,,	8·6	6·51
Manganese	II.	55·	27·5	,,	8·0	3·438
Cobalt	II.	59·	29·5	,,	8·6	3·48
Iron	II.	56·	28·0	,,	7·86	3·56
Nickel	II.	58·7	29·35	,,	8·9	3·298
Aluminium	III.	27·0	9·0	,,	2·6	3·46
Chromium	III.	52·1	17·37	,,	6·5	2·67
Palladium	II.	106·	53·8	,,	11·4	4·67
Iridium ...	II.	193·1	96·55	,,	21·15	4·56
Copper......	II.	63·4	31·7	,,	8·92	3·55
Gold.........	III.	197·3	65·77	,,	19·32	3·40
Rhodium ...	III.	108·5	84·5	,,	12·10	2·85
Platinum ...	IV.	195·0	48·75	,,	21·5	2·267
Silicon......	IV.	28·4	7·1	,,	2·39	2·97
Boron	III.	11·0	3·66	,,	2·5	1·466
Carbon......	IV.	12·0	3·0	,,	2·3	1·30
Bismuth ...	III.	208·9	69·63	,,	9·8	7·105
Antimony	III.	120·0	40·00	,,	6·71	5·96
Arsenic ...	III.	75·0	25·00	,,	5·73	4·368
Phosphorus	III.	31·0	10·33	,,	1·83	5·648
Tellurium	II.	125·0	62·5	,,	6·40	9·76
Selenium ...	II.	79·0	39·9	.,	4·50	8·866
Sulphur ...	II.	32·06	16·03	,,	2·07	7·74
Iodine	I.	126·85	126·85	Liquid	4·004	31·68
Bromine ...	I.	79·95	79·95	,,	3·15	25·38
Chlorine ...	I,	35·45	35·45	,,	1·33	26·65

The numbers in this table are consistent with the results in Tables 58 and 59, showing that when the molecules of a solid metal are further asunder the metal has greater electromotive force.

By previous measurements (Experiments 150, 160, 170, 180, 201, 213, 223, 238, 249, 251), I have shown that the smallest increase of *mean* amount of electromotive force by dilution of metals was often with gold, which is one of the metals having the smallest equivalent volume ; and nearly all the instances in the above table, and in the previous ones, support the conclusion that those metals and metalloids which have large equivalent volumes are those which excite great electromotive force and chemical energy when in mercurial or in aqueous solution, but silver is an apparent exception ; the latter circumstance, and the small amounts of difference between the equivalent volumes of chlorine, bromine, and iodine, together with other minor irregularities, suggest that some additional circumstance besides equivalent volume (probably the relative directions of molecular motion of the two united substances), affects the results.   The greatest increases also of *mean* electromotive force by dilution of electrolytes were with the halogens, and in cases of dilution of metals, with potassium and sodium, both those groups of substances having large equivalent volumes. The small electromotive forces of carbon, boron, silicon, and the heavy metals, indicate condensed molecular groups in the interior of those substances ; and the coincidence of small equivalent volume and electromotive force of those bodies, with that of small electromotive force of neutral saline electrolytes, suggests the idea that both are due to the same fundamental cause, viz., smaller molecular freedom and velocity, and that a more intimate degree of union exists between the atoms or molecules of the heavy metals, etc., than between those of the halogens or of the light metals, and that this degree is usually larger in proportion as the electromotive forces and equivalent volumes of the substances are less.   The same general truth of increase of energy with increase of volume,

probably includes the well known facts that substances usually have greater chemical energy in the gaseous state than in the liquid one, and in some cases when they occupy a larger space by rise of temperature. The results of Experiment 2 (where the volume of diluted bromine was 175·4 times larger than that required by dense bromine vapour), when compared with those of Expt. 4, show that by decreasing the volume occupied by the bromine to one 300th part, notwithstanding the number of molecules in contact with the positive metal was nearly 300 times greater, the *mean* electromotive force was only increased from 1·127 to 1·30 or 2·36 per cent.

As volta-electromotive force is thus related to the equivalent volumes of elementary substances, it is also necessarily connected with the atomic and molecular volumes and weights of those bodies ; and as the specific heats of the elements are related to their atomic weights, and the latter are connected through the equivalent weights and volumes with their electromotive forces, their specific heats must also be related to those forces ; these relations also necessitate a connection between volta-electromotive force and the periodic law.

Influence of Atomic Weight upon Change of Mean Amount of Electromotive Force by Dilution.

The relation of change of *mean* electromotive force by dilution to the atomic and molecular weights of the substances employed, is evidently less simple than to their volumes and molecular distances. With the chlorides of potassium, sodium, and lithium, and of barium, strontium, and calcium (Table 8), with the positive metals magnesium, zinc, and cadmium (Table 20), and with the diluted amalgams of those three metals (Table 44), the magnitudes of the changes of *mean* electromotive force varied *directly* as those of the atomic and molecular weights. But with solutions of chlorine, bromine, and iodine (Table 1), of their acids (Table 5), and of their potassium salts (Tables 8 and 9) ; with magnesium, zinc, and cadmium, as positive metals in water (Table 36), in dilute hydrochloric acid (Table 37), and

solution of potassium chloride (Table 38), and with the sulphates of those metals (Table 8), the variation of *mean* electromotive force was *inversely* as those weights. In some cases the relations of those two series of magnitudes were reversed on substituting a silver negative plate for a platinum one. (See Tables 10, 11, 20, and 21.) It is probable that all these opposite effects were due to the same cause acting under different conditions. For additional data on this part of the subject, see " A Method of Measuring Loss of Energy due to Chemical Union, etc." (Phil. Mag., January, 1892, p. 28.)

Relation of Volta-Electromotive Force to Heat.

This branch of the subject I have not experimentally examined (see p. 83). It is well known that each 30,000 centigrade gramme units of chemical heat produced at the positive plate of a voltaic cell equal one volt of electromotive force ; in some cases, however, a portion of this heat does not appear to be attended by voltaic current. (See " Experimental Verification of the Reciprocal of Faraday's Law of Definite Electrochemical Action," by M. B. Renault, Ann. de Chem. et de Phys., 1867, p. 137 ; and " Some Relations of Chemical Corrosion to Voltaic Current," Proc. Roy. Soc., 1884, vol. xxxvi., p. 331.) It has also been shown that the liquefaction of an alloy by heat is accompanied in some cases by a large and sudden increase of volta-electromotive force (" Changes of Voltaic Energy of Alloys during Fusion," Phil. Mag., July, 1891, p. 27) ; but this may be chiefly attributed to increased freedom of molecular motion. And it is further well known that " most salts, hydrated or anhydrous, dissolve in water with absorption of heat," and " those which absorb heat on solution, do also on dilution " (Watts's Dictionary of Chemistry, 3rd Supplement, p. 990), and this agrees with their increase of electromotive force by dilution, but there are many exceptions to this state-ment if it is applied to all other electrolytes. It is also probable that the enlargement of volume of metals and electrolytes by rise of temperature is attended by increase of electromotive

force, but in such cases it is disguised by simultaneous increases
of molecular activity of a less simple kind produced by the heat.
In a case of pure dilution there is no chemical change, and but
little alteration of total volume of the two substances, and the
molecules are probably simply separated farther asunder by
the diluent, but the effect of heat appears to be usually less
simple than this, and in many cases is attended by chemical
change, and probably alters the relative directions of the mole-
cular movements.   Notwithstanding most strong acids and
alkalies evolve heat by dilution, they increase in electromotive
force.   The changes of electromotive force are, no doubt,
intimately connected with those of latent heat, and every sudden
change of such force and of molecular distance by dilution is
probably attended by disturbance of the ether and by radiation
of energy.

Influence of Contraction of Total Volume during Mixing.

We know that during the chemical union of solid or liquid
substances, a small amount of contraction of volume usually
occurs, and that the volume of the product is usually a little
less than that of the united volumes of its constituents ; and
similarly "when an aqueous solution is mixed with water, con-
traction takes place, *i.e.*, the volume of the solution is less than
the sum of the volumes of the constituent liquids " (Watts's
Dictionary of Chemistry, 2nd Supplement, p. 600).   Favre and
Valson found on dissolving an equivalent weight in grammes of
an anhydrous salt in 1,000 grammes of water, that out of 33
salts 30 gave a small contraction of total volume, but a larger
volume than that of the water alone ; the 3 halogen salts of
ammonia gave a small total expansion (*ibid.*, 3rd Supplement,
part ii., p. 984) ; other investigators have obtained similar results.
(See " Changes of Electromotive Force, Volume, and Tempera-
ture by Mixing Electrolytes," Proc. Birm. Phil. Soc., vol. viii.,
p. 23.)   In the present research the effects of such contractions
were so small in comparison with those of the enlargements of
volume by dilution that they were not observed, and the chloride

and bromide of ammonium gave the usual increases of electro-
motive force by dilution.   Great chemical changes and altera-
tions of internal structure of bodies often occur without much
alteration of volume ; alterations of total volume, therefore,
afford much less information respecting the internal nature of
substances than the changes of *mean* electromotive force.

Influence of the Presence of Hydrates in Solution.

The following measurements were made with a cadmium
platinum couple of the *mean* electromotive forces of a series of
mixtures of concentrated sulphuric acid and water, to ascertain
whether the second and third hydrates of that acid, viz.,
H^2SO^4, H^2O, and H^2SO^4, $2H^2O$, existed in solution.   All the
mixtures were at about a temperature of 14°C.   The two
hydrates are indicated by asterisks.

TABLE 64.—*Solution of H^2SO^4.*

Electrolyte.	Simple E.M-F.	Calculated Mean E.M.F.	Change of Mean E.M.F.	Per cent.
H^2SO^4	1·2790			
$6\ H^2SO^4 +\ 3\ H^2O$	1·2790	1·2435	Gain ·0355 =	2·85
$6\ H^2SO^4 +\ 4\ H^2O$	1·2647	1·2336	,, ·0311 =	2·52
$6\ H^2SO^4 +\ 5\ H^2O$	1·2589	1·2220	,, ·0369 =	3·01
$6\ H^2SO^4 +\ 6\ H^2O*$	1·2398	1·2124	,, ·0274 =	2·25
$6\ H^2SO^4 +\ 7\ H^2O$	1·2303	1·2030	,, ·0273 =	2·26
$6\ H^2SO^4 +\ 9\ H^2O$	1·2246	1·1863	,, ·0383 =	3·22
$6\ H^2SO^4 +11\ H^2O$	1·2218	1·1270	,, ·0948 =	8·41
$6\ H^2SO^4 +12\ H^2O*$	1·2189	1·1642	,, ·0547 =	4·7
$6\ H^2SO^4 +15\ H^2O$	1·2103	1·1441	,, ·0662 =	5·77
H^2O	·85			

The electromotive forces were not variable.

Except in the case of the mixture $H^2SO^4 + H^2O$, where a
slight diminution of gain of *mean* electromotive force occurred,
the results showed no signs of the two hydrates of sulphuric
acid existing as such whilst in solution ; probably they begin to
form only at temperatures approaching that of their separation
in the solid state.

SUMMARY OF RESULTS AND CONCLUSIONS.

By adding together the whole of the percentage gains of *mean* electromotive force, their magnitudes likewise, and of the losses similarly, the proportion of gains to losses was about 100 to 16·4; of average magnitudes about 101 to 1; and of total values about 616 to 1 ; the " losses " were probably in every case only apparent, dependent upon the kind of positive and negative metal and electrolyte, and in nearly all such cases the diluted solution had a smaller simple electromotive force than the diluent.

The amount of effect of liquefaction and dilution upon the *mean* electromotive force varied chiefly with the kind of positive metal, the kind of negative one, and the kind of electrolyte, and to a less extent with the kind of solvent and diluent, and the temperature and viscosity of the solution. Other experiments have shown that the effects are influenced by the rate of diffusion of the dissolved active substance in its solvent. (See p. 112.) None of these circumstances, however, are the active or essential cause of electromotive force, &c., but only the conditions which enable it to occur, and which limit its amount. The greater gain of *mean* electromotive force by dilution of metals with mercury, than of acids, &c., with water, (compare Sections C and D with A and B), was probably due to the former being elementary substances whilst the latter were compounds, and had lost much of their energy by previous chemical union.

The chief general conclusions to be drawn from this research are:—

1st.—Liquefying either the electropositive or the electro-negative metal of a voltaic cell by means of mercury, diluting either of these amalgams with mercury, diluting the electronegative ingredient of the electrolyte by means of water or alcohol, or diluting or separating farther apart the mole-cules of the solid positive metal by means of another solid metal, increased the electromotive force and chemical energy of the substance diluted and consequently also the *mean* electro-

motive force of that substance and of its diluent, provided that in all cases no chemical union occurred between the two substances. Or, more briefly, and including the evidence supplied by the elementary substances (p. 128), *any circumstance which separated the molecules of a metal or electrolyte farther asunder without producing chemical change usually increased the electromotive force of the substance, and the amount of such increase varied with each different substance.*

2nd.—The more strongly united chemically the electropositive and electronegative constituents of an electrolyte or the two metals of an alloy were to each other, the less usually was the electromotive force of the diluted substance. Dilution when attended by chemical union of the diluted and diluting substances, decreased the *mean* amount of power of the two bodies to excite electromotive force when used as an electrolyte or as an alloy in a voltaic cell, because they had by such union already lost some of their energy.   (See also Phil. Mag., Jan., 1892, p. 28.)

3rd.—The stronger the electromotive force and chemical energy of a substance, the greater usually was its increase of electromotive force on liquefaction or dilution.   The gains were usually greater with halogens than with acids, with acids than with salts, with base metals than with noble ones, and with alkali metals than with either, and larger with simple alloys than with chemically combined ones as the positive metal.

4th.—Various experiments made to test the effects of a *series* of dilutions of an electrolyte with water (Tables 3 and 4), of an amalgam with mercury (Tables 46 and 47), and of one solid metal by another (Tables 58 and 59), upon the *mean* amount of electromotive force of the two substances, and therefore upon the *actual* electromotive force of the diluted one, showed that the latter varied directly, and, in some cases at least, proportionately, as the degree of dilution.

5th.—By liquefying or diluting the positive metal by means of mercury, or diluting it by means of a solid metal, the electromotive force of the positive metal and of the direct current were increased.

6th.—By liquefying or diluting the negative metal by means of mercury, the positive electromotive force of the negative metal, and the electromotive force of the inverse or polarisation current were increased.

7th.—By diluting the negative ingredient of the electrolyte at the positive plate by means of water, the electromotive force of that ingredient and of the direct current, and the *mean* of that of the substance and its diluent were increased.

8th.—By diluting the dissolved electronegative ingredient at the negative plate similarly, the electromotive force of that substance and of the inverse current, and the *mean* of that of the substance and its diluent, were increased.

9th.—By diluting the electrolyte at both plates by means of water or alcohol, the electromotive forces, both of the direct and inverse currents, were increased ; the effects of diluting the electrolyte, therefore, were usually less simple than those of diluting either of the metals.

10th.—If by diluting the negative ingredient of the electrolyte, the electromotive force of that substance at the positive plate was increased more than at the negative one, that of the direct current was increased ; but if the reverse it was decreased ; this circumstance explains nearly all the " losses."

11th.—The effect of diluting either the amalgam, or metal, or the electrolyte at the negative electrode was usually much less than that at the positive one, because of the frequently smaller electromotive force and degree of chemical energy of the negative metal ; that metal like the positive one being relatively positive towards the negative ingredient of the electrolyte, but to a much less extent.

12th.—The degree of electromotive force of the actual current obtained varied directly as the amount of *difference* of energy of the opposing molecular motions and electromotive forces at the positive and negative plates.

13th.—Liquefaction and dilution acted largely like a vacuum ; by enlarging the distance between the molecules, it increased probably all the properties which depend upon this,

motive force of that substance and of its diluent, provided that in all cases no chemical union occurred between the two substances. Or, more briefly, and including the evidence supplied by the elementary substances (p. 123), *any circumstance which separated the molecules of a metal or electrolyte farther asunder without producing chemical change usually increased the electromotive force of the substance, and the amount of such increase varied with each different substance.*

2nd.—The more strongly united chemically the electro-positive and electronegative constituents of an electrolyte or the two metals of an alloy were to each other, the less usually was the electromotive force of the diluted substance. Dilution when attended by chemical union of the diluted and diluting substances, decreased the *mean* amount of power of the two bodies to excite electromotive force when used as an electrolyte or as an alloy in a voltaic cell, because they had by such union already lost some of their energy. (See also Phil. Mag., Jan., 1882, p. 38.)

3rd.—The stronger the electromotive force and chemical energy of a substance, the greater usually was its increase of electromotive force on liquefaction or dilution. The gains were usually greater with halogens than with acids, with acids than with salts, with base metals than with noble ones, and with alkali metals than with either, and larger with simple alloys than with chemically combined ones as the positive metal.

4th.—Various experiments made to test the effects of a series of dilutions of an electrolyte with water (Tables 3 and 4), of an amalgam with mercury (Tables 46 and 47), and of one solid metal by another (Tables 58 and 59), upon the mean amount of electromotive force of the two substances, and therefore upon the *actual* electromotive force of the dilute one, showed that the latter varied directly, and, in some at least, proportionately, as the degree of dilution.

5th.—By liquefying or diluting the positive metal of mercury, or diluting it by means of a solid electromotive force of the positive metal current were increased.

lectro-
, such
nd 12),
during
ses of
sion as
me kind
ne.

of *mean*
radation
and the
ng a new
ental and
ry, 1892,

an electro-
nables us to
he molecules
employed for
d mechanical
es of intimacy
metals, alloys,
and of electro-
of delicacy and

e which separates
without producing
omotive force of the
e know that when a
stion, the residuary
and the remaining
freedom and velocity
efaction. This state-
that oxygen, when
d by nitrogen (an inert

such as the electromotive force, degree of chemical energy, amount of chemical heat, &c.   The opposite molecular motions of the metal and electrolyte, appear to be partly converted into purely chemical action and heat, and partly into voltaic action and current, and the proportions so converted seem to differ in every different case.   (Ann. de Chem. et de Phys., 1867, p. 187, M. B. Renault ; and Proc. Roy. Soc., 1884, vol. xxxvi., p. 831.) According to these conclusions, chemical action and electromotive force are coincident effects of molecular motion, and the former is not a cause but only a coincident phenomenon of voltaic current ; it is well known that by various methods, electromotive force and electric current can be produced without chemical action, and chemical union can occur without producing electric current.

14th.—A rise of temperature of the electrolyte from 16° to 80°C. had but little effect upon the amount of increase of *mean* electromotive force by dilution.   (See p. 83.)   If, however, the temperature was sufficient to liquefy the positive metal, a sudden increase of electromotive force due to greater freedom of molecular motion occurred at the period of liquefaction.   (See Phil. Mag., July, 1891, p. 29.)   By dilution, the volume which a dissolved substance occupies in a liquid may be caused to increase until it is much larger than that normally filled by its vapour (see Expt. 2 and note), whilst the range of expansion of a liquid by temperature is comparatively small.   Temperature also appears to act in a very different manner from dilution, and we know it often promotes chemical union.

15th.—The effects of using different kinds of solvents or diluents. such as water, alcohol, mercury, or even solid metals, as a means of separating farther asunder the molecules of the active substance, were substantially the same.

16th.—As pure dilution, either of the metal or of the electronegative constituent of the electrolyte, increased the *mean* electromotive force and energy of chemical union of both, the magnitude of the effect of dilution was not entirely limited by the weakest of the two substances.

17th.—With some diluted solutions, the simple electro-motive forces of which were less than that of water, such as those of alkaline salts and alkalies (see Tables 10 and 12), there was usually a "loss" of *mean* electromotive force during dilution, unless suitable metals were employed. The cases of "loss," however, as much prove the chief general conclusion as those of "gain," because they were often due to the same kind of action at the negative metal as that at the positive one.

18th.—The percentage magnitudes of gain and loss of *mean* electromotive force may be arranged as a continuous gradation order, with the largest gain by dilution at one end and the greatest loss by chemical union at the other, thus forming a new kind of voltaic series, but of a much more fundamental and comprehensive character. (See Phil. Mag., January, 1892, p. 28.)

And 19th.—As the method of measuring the *mean* electro-motive forces of substances in a small voltaic cell enables us to examine to some extent the internal arrangement of the molecules of metals and electrolytes, it may be conveniently employed for distinguishing between chemical compounds and mechanical mixtures, and for ascertaining the relative degrees of intimacy of chemical union and of molecular freedom of metals, alloys, amalgams, metallic mixtures (see pp. 117-121), and of electro-lytes generally ; it also possesses a great degree of delicacy and is easy of performance.

General Remarks.

The general truth that any circumstance which separates the molecules of a substance further asunder without producing chemical change usually increases the electromotive force of the substance, evidently includes gases ; for we know that when a gas or vapour is forcibly rarefied by exhaustion, the residuary portion of it is chilled, absorbs heat, and the remaining molecules therefore must possess greater freedom and velocity of motion than they did previous to rarefaction. This state-ment agrees with the well-known fact that oxygen, when expanded by rarefaction, or when diluted by nitrogen (an inert

gas), unites more energetically with phosphorus, notwithstanding the diluting effect of the nitrogen ; and it is probable that if such cases of chemical union could be examined in a similar manner to the foregoing ones of voltaic action, *i.e.*, if the degree of chemical energy of each of the substances was measured, and the *mean* calculated, the actual chemical energy of union of the substances would be similarly found to increase by dilution and rarefaction. Further, in a special experiment, I found by dissolving one volume of bromine vapour in one volume of water, and diluting the solution to 1,000 volumes, a gain of mean electromotive force of 21·8 per cent., with a $Zn+Pt$ couple. (See also Experiment 2 and note.)

The probable reasons why so extensive a generalisation as that of universal increase of volta-electromotive force with molecular distance has been overlooked are, first, because of its being disguised by the circumstance that when a solution of an acid or salt is diluted with water, the simple electromotive force of the mixture is very often smaller than that of the less diluted substance ; and, second, because the *mean* electromotive force has usually not been considered, and no correction has been made for the electromotive force of the water. The changes of *simple* electromotive force of the *mixtures* have been studied, but the *mean* electromotive forces of the *ingredients* and the *actual* ones of the *individual constituents* have been largely omitted. As out of 108 instances of solutions of electrolytes in Sections A and B of this research, 86 gave *losses* of *simple* electromotive force by dilution ; and out of 105 cases of liquefaction and dilution of metals by mercury in Sections C and D, 64 gave *losses* of such force, it is evident that of neither of those classes of mixtures would it be correct to say that the simple electromotive force " always increases by dilution." (See " The Electromotive

---

NOTE.—This Experiment and Nos. 2 and 4 show that a suitable substance, such as bromine, may occupy, when dissolved, a volume less than that of its vapour at 17°C. and 760 mm. pressure, and may by dilution and without the application of heat, be caused to gradually expand to an indefinite extent without undergoing the *sudden* changes of volume and latent heat due to change from a liquid to a vaporous state.

Force of Metallic Salts," Chemical News, vol. li., page 292, and vol. lii., p. 5.) For *curves* representing the variations of simple electromotive force caused by a series of dilutions of mixtures. (See " A New Method and Department of Chemical Research, Etc.," Phil. Mag., May-Dec., 1890).

It might be supposed, as dilution of the positive metal or of the electrolyte diminishes the number of molecules of each of those substances which at any given moment strike each other per unit of surface, that this would *diminish* the actual electromotive force of the diluted substance ; but it was found that, although by diluting a solution of bromine to nearly 300 times its bulk, the simple electromotive force of the solution was decreased from 1·98 to 1·61 volt. (see Experiments 2 and 4), the *mean* of that of the bromine and water was augmented, and therefore the *actual* electromotive force of the bromine alone was *increased.* It is well known that enlarging the positive plate of a voltaic cell, and thereby increasing the number of its collisions with the negative substance, does not much affect its electromotive force. It is not the number of molecular collisions, therefore, but the *velocity of molecular motion*, which most affects the electromotive force.

The water of dilution added to an electrolyte affected the mean electromotive force in two opposite ways. First, by simply diluting a solution of greater energy than itself, it usually produced a mixture having less electromotive force than the original one ; and, second, by enlarging the volume and thus permitting greater freedom and velocity of motion, it increased the *actual* electromotive force of the dissolved substance and the *mean* of that of the mixture ; and in many cases the simple electromotive force of the mixture was even greater after dilution than previous to it. (See pp. 97-118.) As no sign of increased electromotive force of the water was observed in any case, and as the bulk of the active substance to that of the water was small, its dilution effect in increasing the electromotive force of the water must also have been small.

THEORETICAL CONSIDERATIONS.

The results in general agree with the view that in cases of pure dilution, the molecules of the active substances are simply separated farther apart without their directions of movement being changed or their motions neutralised ; but that in proportion as the added or diluting substances chemically unite with the diluted ones, the directions of movement of the molecules of each are altered, the molecules aggregate into groups, more or less of their motion is neutralised, heat is usually evolved, contraction of total volume frequently occurs, freedom of molecular motion, and the *mean* amount of electromotive force are nearly always largely diminished, and these changes, and the coincident ones of other properties which simultaneously occur, differ with every different substance. The fact that even a neutral salt excites electromotive force indicates that during its formation a portion only of the molecular motion of each of its ingredients is neutralised.

A large number of the results of this research, especially those of dilution of acids and salts, appear to agree with the theory of dissociation, because the most energetic substances usually yield the greatest gains of electromotive force by dilution ; but as that theory, in order to include the whole of the results, would require not only the dissociation of compound substances, but also that of the halogen elements, by simple dilution with water, and the whole of the simple metals by dilution with mercury and even with solid metals (see Tables 58 and 59), I have preferred to employ the simple explanation of increase of volume and of molecular distance and velocity as including the cause of increased volta-electromotive force and current. As dissociation is not energy, it cannot be the cause of electromotive force or current.

Nearly all cases of chemical action agree with the theory that the molecules of all substances are in a ceaseless state of motion, and that chemical union and chemical heat are due to neutralisation of opposite molecular movements of the uniting bodies ; similarly, all the results of this research compel us to

adopt a mechanical explanation of voltaic action. The circumstance that an increase of freedom and velocity of molecular motion of *either* of the uniting substances by dilution (see pp. 97-105), is itself sufficient to augment the *mean* electromotive force and chemical energy of *both*, is conspicuously similar to the augmented violence of collision and amount of heat evolved by two colliding solid bodies when the velocity of only one of them is increased. As it is evident that dilution cannot add to the mass or weight of the active molecules, it can only add to their exciting power by altering their direction or increasing their velocity of motion ; and as energy cannot be created, the increased velocity is probably due to absorbed heat. The latter statement is supported by many well-known facts. In the case of strong acids and alkalies, where heat is *evolved* and the electromotive force simultaneously *increased* by dilution, it is probable that a portion of the heat set free by contraction of the total volume is reabsorbed to satisfy the increased molecular velocity.

According to these views the essential cause of voltaic action is opposite molecular movements of the positive metal and the negative ingredient of the electrolyte ; and the necessary condition of conversion of such motion into volta-electromotive force and current, and the attendant chemical action, is incompatibility of molecular motion of the two uniting substances ; the existence of electromotive force appears to chiefly depend upon relative direction of the molecular motions, and its degree upon the velocity of the oppositely moving particles, and dilution probably increases the velocity of the whole of the molecular motions of a substance, but only a portion of those motions is converted into current. Increase of volta-electromotive force may therefore be due to increased velocity of the oppositely moving molecules of the two uniting substances. These views are further supported by the well-known facts that the substances which produce the greatest voltaic and chemical energy are usually those elementary bodies which possess the most opposite essential properties, and that

after their chemical union, a portion of energy of chemical union still remains. The phenomena, however, are much more complex than these simple ideas indicate; and each degree of electromotive force is probably a result of a concrete collection of simultaneous mechanical impulses of the molecules, each having a different amplitude of motion.